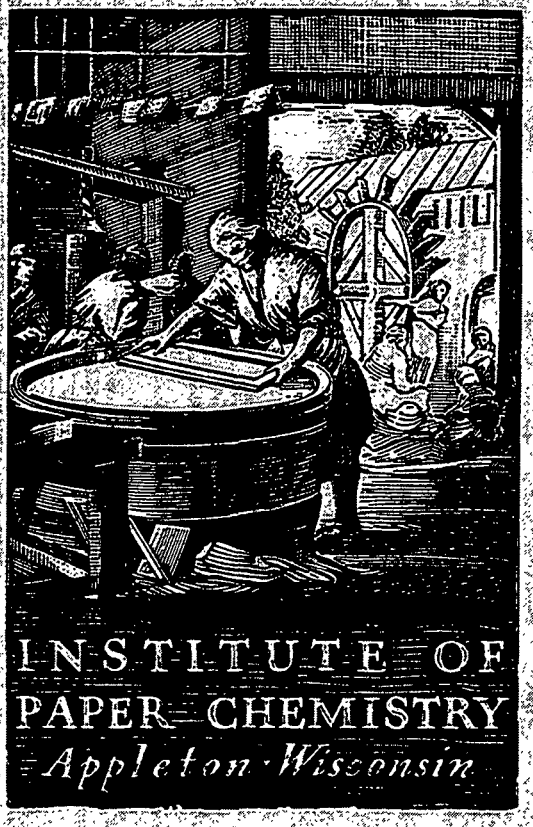

A FUNDAMENTAL STUDY OF THE MECHANISMS OF ACTION OF POLYMERS AS RETENTION AND DRAINAGE AIDS

Project 3276

Report One

A Progress Report

to

MEMBERS OF PROJECT 3276

March 10, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF THE MECHANISMS OF ACTION OF POLYMERS AS RETENTION AND DRAINAGE AIDS

SUMMARY

The use of polymers in papermaking as retention and drainage aids has steadily increased in recent years. To gain optimum efficiency from these materials, a better understanding of the mechanisms of retention and drainage and the accompanying role of polymer structure is necessary. The program described in this report was initiated to extend our understanding of the mechanisms by which polymers mediate retention and drainage. In later stages of the project the possible factors leading to system upsets will be delineated and methods of control will be established.

This report describes the initial work on the mechanisms of retention and drainage enhancement. A series of cationic polyelectrolytes of varying structure (molecular weight, charge density, backbone stiffness, and chain geometry) were examined. To more closely simulate the time scale, consistency level, and drainage forces present on a paper machine, a new instrument (rapid mixing apparatus) was constructed. It permits measurement of single-pass filler retention with contact times of polymer with the furnish in the range of 0.1 to 100 sec. These times encompass those resulting from the usual points of polymer addition at the wet end.

Nonequilibrium coflocculation was found to be an important factor in the early stages of retention development. Polymers with high molecular weight ($\geq 10^6$ daltons) were much more effective than were the smaller chains in inducing retention at short contact times because of the former's ability to participate in long range bridging.

The coflocculation of filler with fines was found to be the rate-determining step in the retention process. For the agitation levels used here the attainment of maximum retention as a result of the bimolecular collisions required contact times of 20-40 sec.

When polymers of moderate molecular weight were employed, little enhancement of fines retention occurred. In contrast, high molecular weight macromolecules increased fines retention at both short and long contact times which led to improved filler retention. Polymers of lower charge density produced better retention presumably due to their capacity for bridging.

A model for the retention process was developed and used to interpret the experimental results.

The effect of polymer structure on improvement of drainage was examined with both Canadian freeness and filtration resistance measurements. From the latter data the hydrodynamic specific surface area and specific volume can be calculated. The freeness studies indicated that the low charge density, high molecular weight polymer was most effective for increasing drainage. Improved drainage was also observed for a classified pulp indicating that fines coflocculation is not the sole operative mechanism. The values for specific surface area decrease and those for specific volume remain unchanged as drainage increases. The latter implies that dewatering of the fiber surface regions is not responsible for the observed changes.

INTRODUCTION

Higher costs of inorganic fillers, and societal pressures leading to increased white water recycling make necessary the use of polymers to increase retention of fillers and fines in the sheet. The rise in fixed production costs induced by inflation requires more efficient production to ensure a profit. Polymer drainage aids can improve the efficiency by increasing paper machine speed or by decreasing energy requirements in the driers.

The polymers themselves are expensive — commonly $1.00 to $1.50 or more per pound — and, when used at the usual dosages of 1-3 pounds per ton of pulp, must perform well to be economically justifiable. However, most of the technical expertise for utilizing these polymers can be characterized as rather vague rules-of-thumb. These are often of little help when starting up a new system or when dealing with a system upset.

Project 3276 was undertaken to develop the basic knowledge necessary to gain the maximum benefit from the use of these expensive materials. The objectives of this program are:

1. To extend the understanding gained in Group Project 3143 of the mechanisms by which polymeric additives function as flocculation or retention aids;

2. To establish mechanisms of polymeric effects on drainage and wet pressing;

3. To determine those major parameters which cause variability in the effectiveness of polymers as retention or drainage aids; and,

4. To establish methods of control of major variables in order to optimize the utilization of such additives.

To meet these goals, the program is being carried out in five phases:

I. Mechanisms of filler and fines retention by polymers;

II. Mechanisms of drainage enhancement by polymers;

III. Means for optimizing optical properties;

IV. Effects of other components common to paper furnishes; and

V. Factors causing variations in retention and drainage, and methods for control.

The program has a total budget of $190,000 over a two-year period starting May 1, 1975. Phases I and II are being pursued during the first year. The remaining phases will be addressed during the second year.

This report covers the initial attack on Phases I and II. Because the time from application of a polymer retention aid to sheet formation is very short (typically less than one minute) while the usual laboratory evaluation procedures require many minutes, a lack of correlation between mill and laboratory results is often found. The approach taken here was to devise an apparatus to more closely simulate machine operating conditions. The objective is to study in detail the several processes leading to retention over the short time scale. The effect of polymer architecture on retention is examined with particular attention being paid to the charge density, molecular weight, backbone flexibility, and chain geometry of the macromolecules.

The approach to understanding the role of a polymeric drainage aid in improving drainage was to study its effects on the basic properties of the pulp. Here, also, the dependence on polymer architecture is being examined.

Because of the different techniques used in the retention and drainage studies, the two topics are treated separately in this report.

EXPERIMENTAL MATERIALS AND THEIR CHARACTERIZATION

PULPS

Samples of a bleached northern softwood kraft pulp were beaten at 2% consistency in a Valley beater to four levels of freeness. A portion of each beaten pulp was classified by passing twice at a consistency of 0.03-0.05% over the IPC Web Former on a 70 x 48 mesh wire. The classified and remaining portions of the unclassified pulps were dewatered to 25-30% solids on a basket centrifuge, treated with 1/2% of formaldehyde to retard bacterial growth and stored at 5°C. The white water from the two passes was combined and concentrated by settling and decanting to about 1/2% solids. These white water samples from the four levels of beating were also treated with 1/2% formaldehyde and stored at 5°C. The Canadian Standard Freeness of the several pulps in deionized water are presented in Table I.

TABLE I

FREENESS OF PULPS

Pulp No.	CSF, ml	
	Whole	Classified
1	635	735
2	435	685
3	340	605
4	195	515

Pulp No. 1 was slushed in the Valley beater with no bedplate load and represents the original unbeaten pulp.

Samples of Pulp No. 3 (whole) and Pulp No. 4 (whole) were classified on the Bauer-McNett classifier. The average percentage of the pulp passing through the screens of a given mesh for duplicate runs was as follows: 20 mesh,

40.0%; 35 mesh, 24.4%; 65 mesh, 16.8%; and 150 mesh, 11.7% for Pulp No. 3; and 20 mesh, 45.8%; 35 mesh, 30.0%; 65 mesh, 20.2%; and 150 mesh, 12.1% for Pulp No. 4.

POLYMERS

Six different cationic polyelectrolytes were chosen to encompass a range of polymer architecture. The major parameters were molecular weight, charge density, chain linearity and backbone stiffness. The various samples differed, of course, in their detailed chemical composition. A study of this latter factor is beyond the scope of the present investigation. Because the major interaction between the polymers and the negatively charged surfaces of fiber and pigment is electrostatic in nature, it is believed that the particular chemical composition of the samples is of secondary importance.

Sample T100 is a homopolymer of a tertiary amine hydrochloride while T5 is a copolymer containing about 5 mole% of this tertiary amine and 95 mole% of acrylamide monomer. Because of the chain transfer properties of polymerizing tertiary amines, these samples have only moderate molecular weights.

Sample Q100 is a homopolymer of methacryloxyethyl trimethylammonium methosulfate while Q5 is a copolymer with about 5 mole% of this quaternary ammonium monomer and 95 mole% of acrylamide monomer. The molecular weights of these samples are in the range of one to several million. The homopolymer has previously been shown to be a good flocculant for polystyrene latices (1).

Sample P1 is polyethylenimine (PEI), a highly branched (2) polymer containing primary, secondary, and tertiary amine groups in the ratio 1:2:1. The molecular weight of this material is moderate.

Sample C1 is chitosan, a derivative of cellulose with a primary amine group replacing the hydroxyl group at the C2 position on the ring. This material represents a polymer with a rather stiff backbone and is believed to have a molecular weight of several hundred thousand.

The current concept of the mechanism of colloid flocculation by polymer suggests that the extension of the polymer in solution is related to its effectiveness. The most experimentally accessible measure of polymer size is its intrinsic viscosity $[\eta]$, or its ability to enhance the solvent's viscosity. According to the theory of Fox and Flory (3) the intrinsic viscosity is a function of the molecular weight M of the polymer and its radius of gyration $\langle s^2 \rangle^{1/2}$.

$$[\eta] = \Phi' \langle s^2 \rangle^{3/2} / M \qquad (1)$$

Here Φ' is Flory's universal constant with a value of 3.7×10^{22} when $[\eta]$ is in units of dl/g and s is in cm. The radius of gyration, which is the average distance of a polymer segment from the molecule's center of mass, is a function of the thermodynamic interaction between the polymer and solvent and also is a function of the charge density. The latter factor causes mutual repulsion between charged groups along the chain backbone thereby increasing the polymer's size. Equation (1) may be rewritten as

$$[\eta] = \Phi' (\langle s^2 \rangle_o / M)^{3/2} M^{1/2} \alpha^3 \qquad (2)$$

where the quantity in parentheses is a constant for a given polymer and α is the expansion factor.

$$\alpha = f(\text{polymer-solvent interaction, charge density})$$

The variation in polymer-solvent interaction among the various systems studied here is likely to be small compared to the effect of charge density. As

polymer-solvent interaction and charge density go to zero, α approaches one. Thus, from Equation (2) it is seen that the intrinsic viscosity is primarily a measure of molecular weight ($M^{1/2}$) and charge density (α). By adding an excess of simple electrolyte (NaCl), the effect of mutual repulsion can be negated by a screening effect, and the polymer molecule assumes a much more compact configuration. In this case α is reduced toward one and the intrinsic viscosity is governed chiefly by molecular weight.

The intrinsic viscosities of the six samples were measured in distilled water adjusted to pH 5 with H_2SO_4 in the absence of added electrolyte and with 0.1N NaCl present. In the former case typical polyelectrolyte behavior was exhibited by all polymers with the reduced specific viscosity increasing non-linearly with decreasing polymer concentration. Reciprocal Fuoss plots (3) yielded linear curves which could be extrapolated to zero concentration to obtain $[\eta]$. For the measurements with added electrolyte the ionic strength was high enough to provide screening of the polymer charges, and the usual linear plot as for nonionic polymers was obtained. The results are listed in Table II.

TABLE II

INTRINSIC VISCOSITY AND CHARGE DENSITY AT pH 5

Polymer	$[\eta]$, dl/g		Degree of Charge σ
	No Salt	0.1N NaCl	No Salt
T5	0.57	0.28	0.05
T100	19.7	0.41	(0.6)
Q5	64.0	7.1	0.05
Q100	86.0	7.4	1.0
P1	0.73	0.48	0.5
C1	28.0	2.9	(0.6)

Measurements made with no added salt provide information about the relative extensions of the various molecules under the conditions obtaining in the retention and drainage studies to be described later. As outlined above, the data with added salt allow comparison on the basis of molecular weight disassociated from charge density effects. The magnitude of the latter effect may be seen by comparing the results at the two ionic strengths for T100 and C1, both highly charged molecules. In contrast the results for T5 and P1 show a lesser effect. For the latter polymer this is because its highly branched nature prevents the large expansion available to T100 and C1. The approximately equivalent changes for Q5 and Q100 in going from low to high ionic strength are not readily explained. In keeping with the results for the T series the change for Q100 would be expected to be much greater than for Q5. The answer may lie in the presence of differing amounts of non-Newtonian flow for these two samples. The existence of non-Newtonian flow for some very high molecular weight polymers ($> 10^6$ daltons) is well documented but was not investigated here. The relatively large values for C1 (for its purported molecular weight) at both ionic strengths is likely a manifestation of this polymer's chain stiffness which is embodied in the factor in the parentheses in Equation (2).

The degree of charge σ (defined as the fraction of all monomer units carrying a positive charge) of the samples at a pH of 5 is also listed in Table II. The quaternary ammonium salts Q5 and Q100 may be presumed to be completely ionized at this pH. Thus, their charge density corresponds to their composition. Likewise, by analogy to simple amines it can be expected that all the tertiary amine groups on T5 are protonated at pH 5.

As the density of amine groups along a chain is increased, it becomes more difficult to protonate groups residing adjacent to groups that are already charged. This neighboring group effect is well-known (4). For polyvinylamine $-(CH_2-CHNH_2)-_n$ potentiometric titration reveals a degree of protonation at pH 5 between 0.58 and 0.71 (4,5), the latter corresponding to higher concentrations than are under consideration here. It is expected that the linear polymers T100 and C1 would behave similarly to polyvinylamine toward protonation and a value of 0.6 has accordingly been assigned to them in Table II. (This value may be slightly low for C1 since the amine groups are more widely spaced along the chain backbone for this polymer than for T100 and polyvinylamine, thereby reducing slightly the charged neighbor effect.)

Because of the presence of amine groups of different degree in polyethylenimine, the protonation curve (as a function of pH) for this polymer differs appreciably from that for polyvinylamine (5). In addition to the difference in chemical groups it is conjectured (6) that the highly branched nature of PEI further restricts the protonation by the rather close proximity of non-neighboring charged groups. Values for the degree of protonation for PEI at pH 5 range from 0.49 to 0.58 (5,6) with the former corresponding more closely to the concentrations used in this study.

To recapitulate, the characteristics of the six polymers may be described as follows:

1. All but P1 are linear.
2. The charge densities may be delineated as follows:
   T5 and Q5 — low; P1, C1, and T100 — moderately high;
   and Q100 — high.

3. All but C1 have C-C backbones with moderate flexibility. The former with the β-1,4 glycosidic linkage of the pyranose rings has the enhanced backbone stiffness characteristic of cellulosics.
4. The molecular weights are: Q5 and Q100 — very high; C1 — high; and T5, T100, and P1 — moderate.

TiO_2

A 73% solids dispersion in distilled water of RG-grade (The Glidden Company) titanium dioxide (anatase) was prepared in accordance with previous work (7) by stirring in a malted milk mixer for 20 minutes. Cooling was provided to prevent excess heating and evaporation of water. The suspension was diluted to 7.5% solids and then stirred vigorously for two hours. Vacuum was applied to remove entrained air and the dispersion was allowed to settle for 24 hours. The fraction consisting of particles smaller than 1.0 μm was siphoned off the top of the partially settled suspension into a polyethylene bottle, and was stored on a rotator to prevent settling and aggregation. The siphoning technique with the tip of the siphoning tube turned upward has been previously described (8).

According to Webb (7) a suspension of this grade of TiO_2 prepared as above will have a number average particle size of 0.130 μm and a weight average diameter of 0.152 μm. A fairly narrow distribution of sizes is indicated by these values and by the fact that 90% of the particles have diameters between 0.094 and 0.207 μm. He also found by electron microscopy that the particles were approximately spherical although with some surface roughness.

RETENTION STUDIES

THE RAPID MIXING APPARATUS (RMA)

Two objectives were foremost in the design considerations for this instrument. First, it was desired that the mixing of the polymer retention aid with the other components of the furnish be carried out in such a way that the distribution of the former throughout the latter be as uniform as possible. This would minimize the uneven treatment or "marbling" that nonuniform irreversible polymer adsorption can lead to. Secondly, a means to form a sheet at a short, reproducible time after mixing the polymer with the furnish was necessary. This "contact time" would need to be variable from as short as practicable up to the order of minutes in order to elucidate the kinetics of the retention process. Subsidiary objectives were that the system not be too complex for routine and rapid operation and that the quality of the formation of the sheets be good for subsequent studies of their optical properties. The instrument that was developed has met all these objectives. For simplicity, it will be broken into its component parts in the description that follows.

The Mixing Tee

The technique of the mixing tee suggests itself as the answer to the requirement for rapid, uniform mixing. This method has often been used (9) for studying the rates of chemical reactions whose half-lives are in the order of seconds or less. A photograph of the tee (T) and associated valves (B) is shown in Fig. 1. The multiport 3/8-inch ball valves are fed by a Masterflex dual-channel tubing pump drawing from two reservoirs. This pump provides constant flow rates which can be varied by a rheostat by a factor of two. In the usual setup pulp plus TiO_2 slurry is placed in one reservoir and the polymer solution in the other. In the "recycle" phase the pump continuously circulates the pulp

slurry and polymer solution via 1/2-inch polyethylene tubing to the valves and back to their respective reservoirs. This is necessary to keep the pulp and TiO_2 from settling out in the valves and tubing between runs. Additional agitation in the pulp reservoir is provided by a Lightnin' stirrer to ensure a homogeneous mixture is obtained. In the "operate" phase the valves direct the flow to the mixing tee and thence to sheet formation.

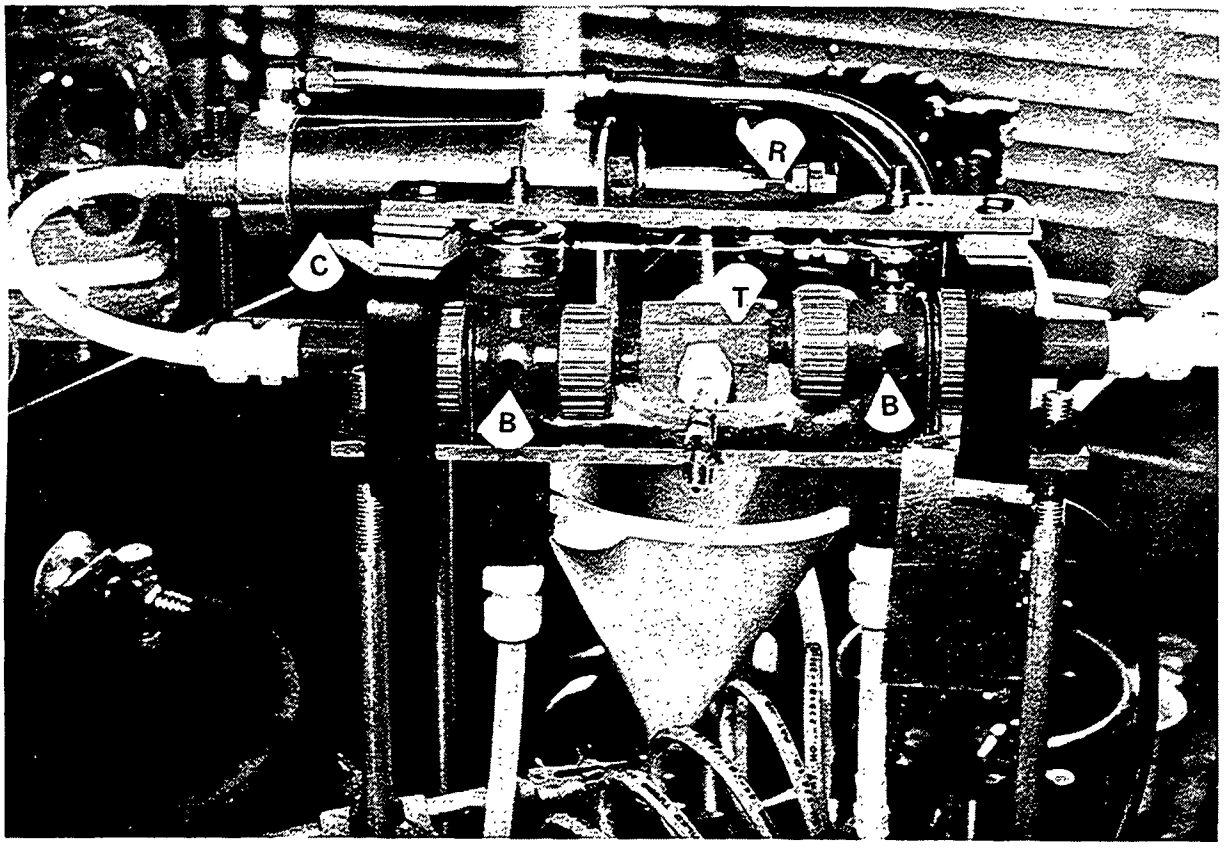

Figure 1. The Mixing Tee and Associated Elements. Parts Designated by Letter are Described in the Text

The tee is a block of nylon with four ports in the horizontal plane. The two 1/4-inch ID ports leading from the two valves are opposed and form the arms of the T. They are displaced slightly with respect to each other in the vertical direction to provide a spiraling motion to the fluid issuing from the

tee. This gives improved mixing of the two components. The third port is connected to 8-mm ID glass tubing leading to the sheet forming zone and forms the trunk of the T. The fourth port is opposed to the third and is plugged during the "operate" phase. The plug is removed for flushing the tee and the connecting arms to the valves between each run. The particular glass tubing (mixing zone) being used in a given run is also emptied and flushed with distilled water between each run to remove any "old" furnish which would contribute a spurious contact time.

The ball valves are turned through 180° synchronously by a cable attached to an air-operated ram (R). Air is supplied to one or the other end of the (Bimba) cylinder (C) by a solenoid so that rotation of the valves in both directions is positively driven and requires a negligible time. The operation of the solenoid in turn is controlled by an electronic timer type 30HL1 (Photoswitch Division, Electronics Corporation of America). This latter unit has four ranges which altogether span the region from 0.1 to 240 seconds. The reproducibility of elapsed time at a given setting is 1-2% depending on the range.

The Sheet Mold

For contact times $\geq$ 1 sec the furnish is conveyed from the output port of the mixing tee via a 50-cm long piece of 8-mm glass tubing to a sheet mold. A photograph of the latter is presented in Fig. 2. A septum (W), 3 inches in diameter, of 150 mesh, bronze wire is surmounted by a Lucite decklebox, the latter being fed by the glass tubing (T) from the mixing tee. The sheet is formed by suction provided by a vacuum filter flask (F). The flask and septum are separated by a quick opening, rubber plunger-type, air-operated valve (V). Air to positively drive the valve open or closed is controlled by a solenoid

(S) which is actuated by a second timer of the same type (30HL1) as described above. Controlled agitation in the decklebox is provided by either manual stirring with a polyethylene paddle in a prescribed reproducible manner, or Lightnin' stirrer with a standard three-blade propeller. This agitation is used only for contact times greater than two seconds and is discontinued 1-2 seconds before application of suction to ensure good formation. As judged visually, this parameter was uniformly good.

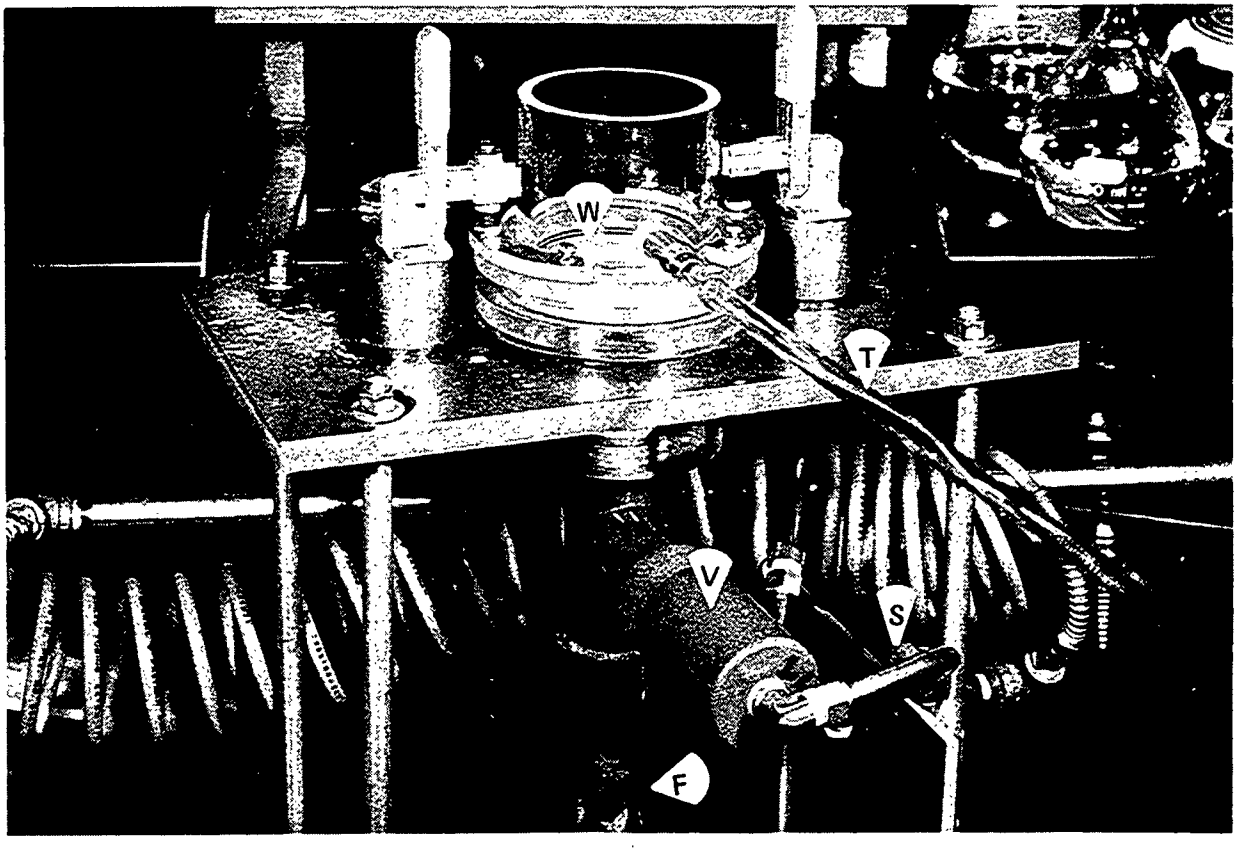

Figure 2. The Sheet Mold Section

A standard suction of 10-inch Hg (135-cm H_2O) was employed. Sheets formed with vacuums of 5, 10, 15, and 20-inch Hg showed (Table III) a regular decrease in retention with increase in suction. However, the change is small, and 10-inch Hg was chosen as representative. Suctions larger than this also tended to cause

loss of white water from the filter flask out the vacuum line due to splashing. It was important to prevent this loss as the composition of the white water was also analyzed.

TABLE III

EFFECT OF SHEET MOLD SUCTION ON RETENTION

(0.1% Pl; 10% TiO_2; contact time, 2.5 sec)

Vacuum, in. Hg	Retention, %
5	36.2
10	34.1
15	33.2
20	31.8

The Moving Wire

Because it required approximately one second to fill the decklebox of the sheet mold at the maximum pump speed, an alternative method was required to gather retention data for contact times less than one second. A moving wire former was devised and is depicted in position with the mixing tee in Fig. 3. The wire (W) is a 2-inch x 24-inch strip of 150-mesh bronze wire. It is drawn at a constant rate across the suction platform (P) by a tow rope hooked to the loop at the leading edge of the wire. The other end of the tow rope is wound up on a spool attached to a Lightnin' stirrer. The Lucite suction platform has a series of six slots over which the wire travels. (The last two of these appear as white rectangles in Fig. 3 just beyond the end of the wire.) Lucite travel guides (G) serve to delimit the sideways motion of the wire. Figure 3 represents the position of the wire at the start of a run with the remainder of the wire draped down between the suction platform and the supporting structure for the mixing tee.

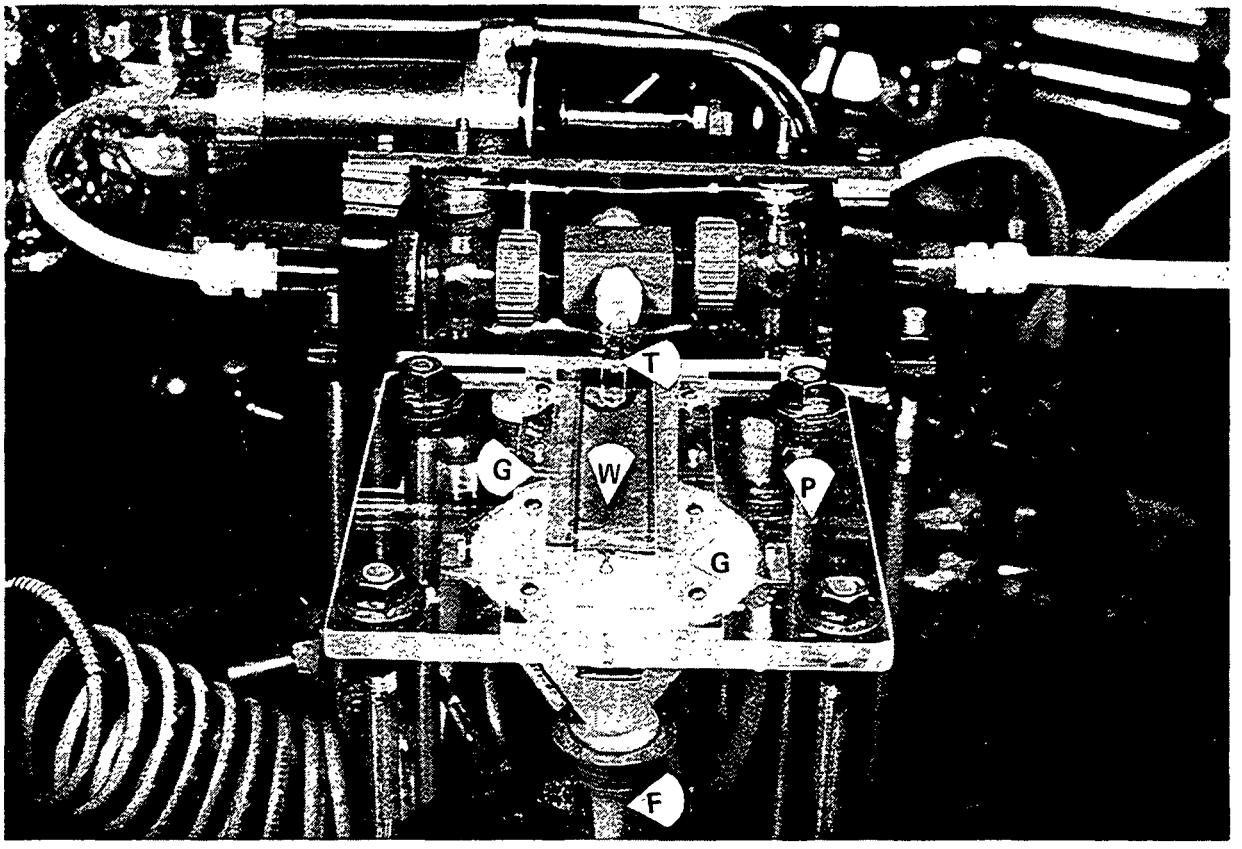

Figure 3. The Moving Wire Section

Suction is supplied by a laboratory vacuum line connected via a filter flask (F) (to catch the white water) to a polyethylene funnel glued to the underside of the suction platform. A run is begun by starting the tow rope take-up and the flow of stock to the mixing tee. By the time the stock reaches the flow spreader, the wire has attained a constant velocity, all suction slots have been covered, and the prewetted wire is pulled down tightly against the slots to provide rapid drainage.

The contact time was changed by variation either of the pump speed or the length of the mixing tube (T). Three of the latter with lengths of about 10, 30, and 100 cm were used. (The 10-cm tube is shown in Fig. 3.) For each an elbow was formed at the end so that the flow of stock was directed at approximately right angles onto the moving wire. Although this design resulted in an

increased loss of pigment through the wire, it allowed a relatively short forming zone and a simple geometry for the flow spreader (approximately circular in cross section). The end of the flow spreader was positioned 1/4 inch above the wire over the first slot in the suction platform. Experiments showed that about 94% of the water drained through the first slot bringing the solids level from 0.25 to 4%. An additional 3% of the initial water present was lost through the second slot to give a web of 8% solids. Little additional drying took place over the remainder of the slots. After leaving the suction platform, the wire was drawn onto a supporting platform (not shown in Fig. 3), and at the conclusion of the timer cycle the tow rope take-up was stopped. The wet web was removed from the wire with a plastic scraper and saved for subsequent analysis.

The flow spreader geometry used here leads to a web with a very uneven basis weight profile across the sheet. The web thickness is greatest along the center line and goes to zero at the edges and, hence, is of no use for optical, strength, or formation studies. It does, however, permit retention experiments at very short contact times for which it was designed.

Analysis of RMA

The timer (T1) controlling the ball valves leading to the mixing tee is operated as an interval timer. It governs the length of time the pump feeds the mixing tee and, therefore, the basis weight of the sheet in the sheet mold mode or the total amount of furnish transported to the wire in the moving wire mode. The other timer (T2) is operated as a delay timer. It is started simultaneously with the opening of the valves to the tee but does not open the valve beneath the sheet mold to allow drainage until the time set has elapsed. It, therefore, governs the contact time before sheet formation. This timer (T2)

is not used in the moving wire mode. The settings on both timers were calibrated by stopwatch.

Two pump speed settings were used to obtain a range of contact times. The corresponding flow rates were calibrated during each series of experiments to correct for the slight day-to-day variation in pump operation. The volume of furnish delivered from the mixing tube during a time set by T1 is used to calculate the flow rate Q in the mixing tube. From this the average bulk velocity $\langle v \rangle$ can be calculated from

$$\langle v \rangle = 4Q/\pi D^2$$

where D is the tube diameter (8 mm). The Reynolds number R_e is defined as $\langle v \rangle D\rho/\eta$ where ρ and η are the density and viscosity of the fluid, respectively, and may be taken here equal to the values for water. Finally, the average residence time of a fluid through a pipe is $L/\langle v \rangle$ where L is the length of the pipe. Typical values for these parameters are listed in Table IV. Average residence times for tubes of other lengths may be calculated by direct proportion. (Flow rates are not affected by the tube length over the range of values used here.) The Reynolds numbers for these flow rates indicate turbulent flow is occurring thereby ensuring continued good mixing along the length of the tube.

TABLE IV

FLOW RATE PARAMETERS FOR RMA

Pump Speed Setting	Q, cm^3/sec	$\langle v \rangle$, cm/sec	R_e	Average Residence Time, sec (10-cm tube)
6	51.2	101.9	8,150	0.098
10	81.2	161.5	12,900	0.062

The average contact time <τ> can be calculated from the timer settings, the dimensions of the apparatus, and the flow rates. The schematic of the RMA in Fig. 4 will aid in the discussion that follows.

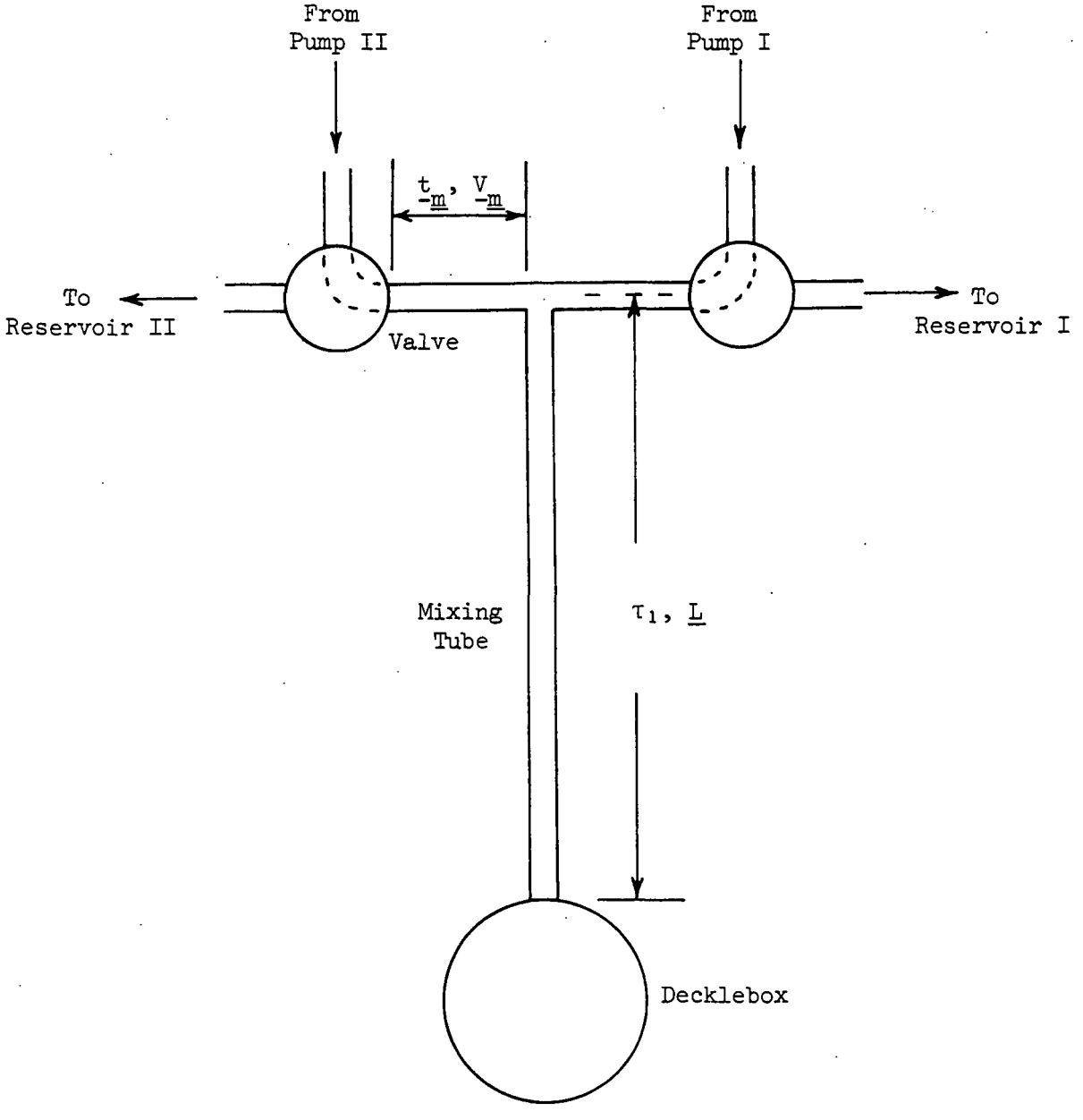

Figure 4. Schematic of the Rapid Mixing Apparatus Showing Dimensions and Parameters Defining its Operation. Valves Shown in "Operate" Position

In the sheet mold mode the timer T1 must be set to furnish enough stock to the decklebox to form a sheet of the desired basis weight.

$$T1 = t_m + \tau_1 + t_f = (V_m/Q) + (\pi D^2 L/4Q) + (W\pi R^2/100\ cQ) \qquad (3)$$

Here V_m is the volume of the arm of the tee, D and L are the diameter and length of the mixing tube, W is the desired basis weight in units of g/m^2, R is the radius of the septum in the sheet mold in cm, and c is the consistency ($g/100\ cm^3$) of the furnish in the mixing tube (equal to half that in Reservoir I). The corresponding times in Equation (3) are, respectively, the time t_m to fill the arm of the tee, the time to fill the mixing tube τ_1, and the time to fill the decklebox with enough stock for the desired sheet t_f after the stock has reached the inlet port in the decklebox.

The timer T2 is set to the sum of T1 plus the time the stock resides in the decklebox between the completion of filling and sheet formation t_d.

$$T2 = T1 + t_d$$

The average contact time $\langle\tau\rangle$ is the sum of three terms.

$$\langle\tau\rangle = \tau_1 + t_f/2 + t_d \qquad (4).$$

These terms represent the residence time in the mixing tube, half the time for filling the decklebox, and the time delay in the decklebox after filling. The term $t_f/2$ is the average for all portions of the furnish in the decklebox and is approximately 0.7 sec for the usual operating conditions; it is negligible at the longer times. The residence time in the mixing tube is typically 0.3 sec which limits the minimum $\langle\tau\rangle$ in this mode to about 1 sec. In terms of the experimental variables it can be readily shown that

$$\langle\tau\rangle = T2 - W\pi R^2/200\ cQ \qquad (5)$$

neglecting the small contribution from t_m (~ 0.04 sec).

In the moving wire mode the timer T1 must again be set to deliver the desired amount of stock to the wire. Typically this is made equivalent to the amount used for sheet formation above and, hence, is given by Equation (3). The average contact time $\langle\tau\rangle$ is the sum of τ_1 and the average time for drainage on the moving wire. The latter can be calculated from the velocity of the wire and the distance over which the bulk of the drainage occurs. As mentioned previously this happens during passage over the first two slots or a distance of 2.9 cm. At a wire speed of 27.5 cm/sec (75 fpm), the average contact time on the wire is ≤ 0.08 sec. Hence

$$\langle\tau\rangle = \tau_1 + 0.08$$
$$= (\pi D^2 L/4Q) + 0.08 \qquad (6)$$

This probably overestimates the average time on the wire since most of the water is drained through the first slot. Thus, $\langle\tau\rangle$ in Equation (6) may be looked upon as an upper limit and may be 0.04-0.06 second high.

It is of interest to calculate the drainage rate $\overline{V}$ through the first slot.

$$\overline{V} = QF/A$$

Here Q is the volumetric flow rate, F is the fraction of the water passing through the first slot and A is the cross-sectional area of the slot. The result is $\overline{V} = 16.5$ cm/sec which is in the range of drainage rates found on a paper machine producing medium weight paper from slightly beaten stock at 1200-1500 fpm (10).

EXPERIMENTAL PROCEDURES

All the retention studies in this report were carried out using pulp No. 3 (whole). A 30-g batch was treated in the British disintegrator for 300 counts at 1-1/2% consistency in distilled water and then diluted to 1/2% consistency. A 4000-ml aliquot of this was placed in Reservoir I of the RMA and an amount of TiO_2 was added to give an add-on rate of 5% on the OD pulp. The pH was adjusted to 5.0 with H_2SO_4 and the mixture was stirred for about 15 minutes before beginning a run. The appropriate amount of polymer (as a 0.1% solution) was added to 4000 ml of distilled water in Reservoir II and adjusted to pH 5 with H_2SO_4. Because equal volumes of pulp slurry and polymer solution are mixed at the tee, the final consistency in the mixing tube is 0.25%.

For comparison with results from handsheet experiments it was desirable to form sheets with the RMA at the same basis weight. For a 2.5-g Noble and Wood handsheet this corresponds to 58.7 g/m^2. The 3-inch diameter sheet formed in the RMA at this basis weight has an OD weight of about 0.25 g. To increase the precision of the measurements, duplicate sets of sheets were formed at each condition and were combined for subsequent analysis. The white water from the duplicates was also combined.

Runs were customarily carried out in sequence from the shortest to the longest contact times. However, some runs were made in reverse order and in random order. No effect of the sequence was found.

Sheets were couched off the septum with a blotter, and were transferred to tared crucibles for drying and ashing. The pulp scraped from the moving wire was similarly treated. White water from either sheet mold or moving wire modes was filtered through oven-dried, tared Whatman No. 40 ashless filter paper.

These were then dried at 105°C, weighed, ashed at 850°C for 1-1/2 hr, and reweighed. From the ovendry and ash weights of the various samples the amount of fiber and TiO_2 in them could be determined. Single pass % retention R was calculated from

$$R = w_a/(w_o-w_a)\ (0.0005) \qquad (\%)$$

where w_a is the ash weight and w_o is the ovendry weight. (The ash weight of the pulp alone was negligible.)

Limited studies of TiO_2 retention in handsheets were carried out. The pulp was disintegrated, diluted to 1/2%, mixed with TiO_2, and adjusted to pH 5 as described above. An aliquot sufficient for one handsheet (2.5 g pulp) was removed to a separate container. The desired amount of polymer was added, the slurry was mixed for one minute with a Lightnin' stirrer, and the sample added to sufficient water in the Noble and Wood decklebox to give the usual forming consistency ($\sim$0.04%). The sheet was formed following the standard procedures and was dried and ashed as above. The contact time in these experiments was estimated to be about 70-80 sec.

Pulp titration studies were carried out as follows. A 25-ml aliquot of 0.5% consistency pulp (no TiO_2) was adjusted to pH 5 with H_2SO_4 and then treated with 25 ml of a polymer solution which had been adjusted to pH 5. Following 60 sec of rapid mixing, the stock was poured through a 100-mesh screen. The resulting white water was centrifuged for 30 sec at about 3000 rpm in a laboratory bench centrifuge, and the supernatant was transferred to the sample cell of a Model B Zeta-Meter (Zeta-Meter, Inc., New York). Electrophoretic mobilities were measured and were converted to zeta potentials (11) using the Helmholtz-Smoluchowski equation.

RESULTS AND DISCUSSION

Operational Parameters

Before describing the main results of this study, the effect of several operating variables will be discussed. To check the reproducibility of the experiments, several series of runs were duplicated and in some cases replicates of runs within a series were made. A typical example is shown in Fig. 5 where retention of TiO_2 (sheet mold mode) is plotted against the logarithm of the average contact time $\langle\tau\rangle$. (For brevity this latter term will be shortened to contact time in all subsequent discussions.) On the average the deviation of the individual measurements from the mean is less than 2% retention. This experiment combines error in RMA operation and in subsequent sheet analysis. Comparison of a series of runs (with the same furnish composition) on separate days reveals negligible day-to-day variability in preparation of materials or RMA operation. Similar experiments with the moving wire mode gave good reproducibility here, also, proving the capabilities of the RMA.

Two methods of providing agitation to the furnish in the sheet mold decklebox after filling were examined. The first was gentle manual stirring with a polyethylene paddle in a prescribed reproducible manner. For the second a Lightnin' stirrer with standard three-blade propeller was positioned in the decklebox and was activated once the latter was filled. Two stirrer speeds were used: 300 and 900 rpm. In both cases (manual or mechanical) stirring was discontinued 1-2 seconds prior to sheet formation. (Otherwise thin areas and, in some cases, holes were formed in the sheet, thereby reducing drainage stresses and apparently increasing pigment retention.)

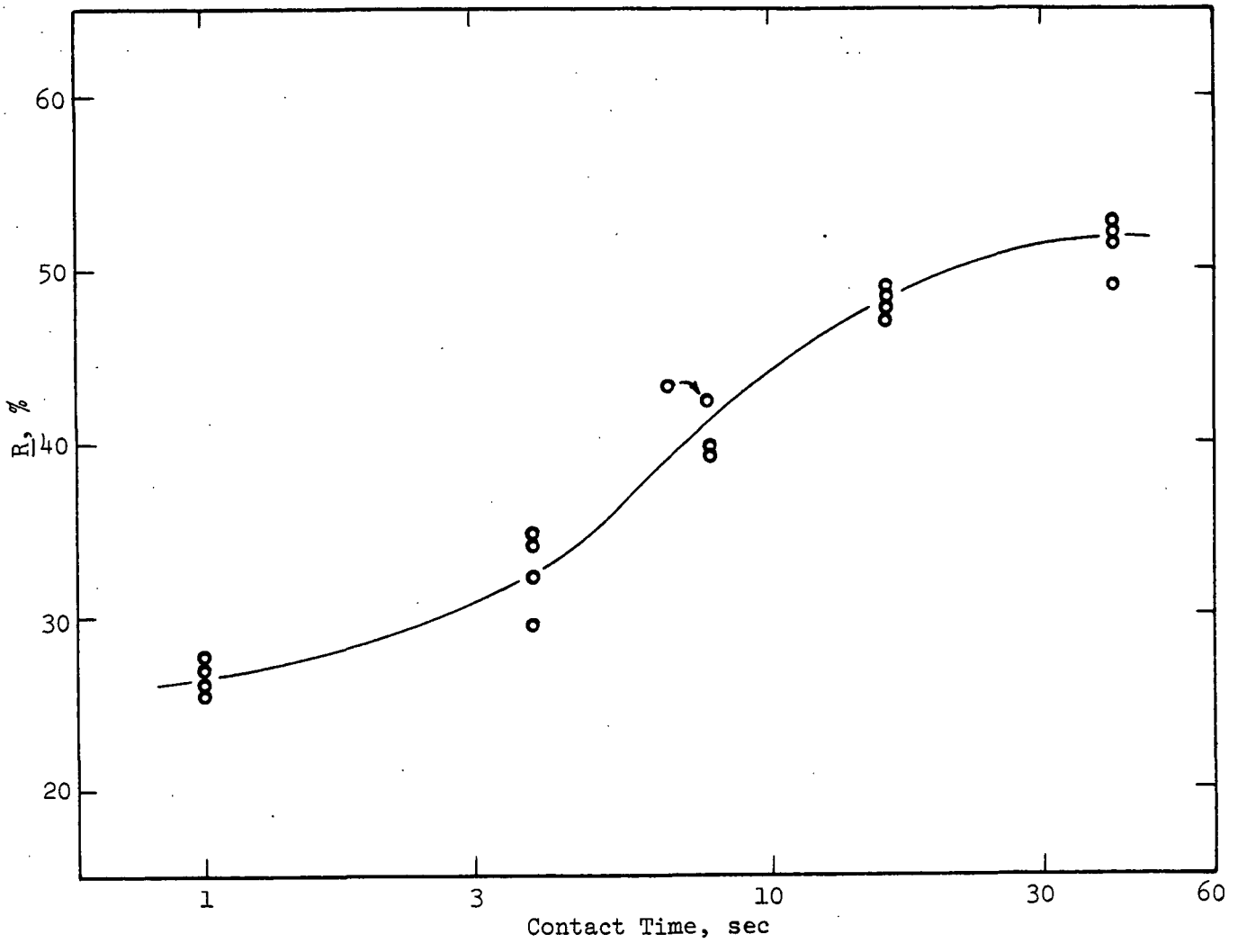

Figure 5. Reproducibility Check of RMA in Sheet Mold Mode. 5% TiO_2. Polymer: 0.1% T5

Experiments to compare the two methods were performed on two different days. The results are presented in Fig. 6 as percentage retention as a function of contact time and stirring method. The difference between the manual method and mechanical stirring at either 300 or 900 rpm is slight. This is surprising because the polymer T5 produced some of the poorest retention (see next section) of the several polymers studied here and, hence, might be thought to form relatively weak coflocculation of fiber and filler. It has been previously shown (12-14) for "dynamic drainage jars" of similar dimensions to the decklebox used

here that a stirring speed of 900 rpm was sufficient to cause greatly reduced retention of either filler or fines. Intuitively, it might be expected that the much gentler agitation provided by the manual method would lead to rather higher retention than would the mechanically stirred case.

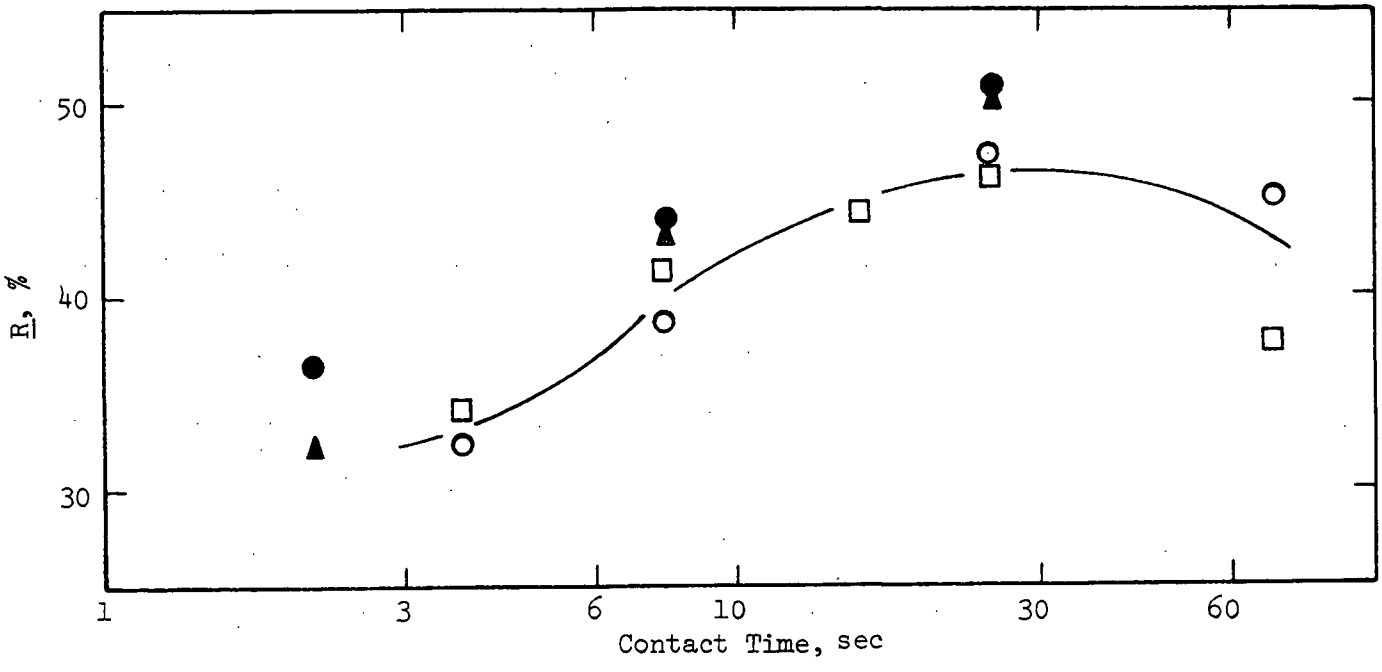

Figure 6. Effect of Rate of Agitation in Sheet Mold. 5% TiO_2. Polymer: 0.1% T5. Circles, Manual Mixing; Triangles, 300 rpm; Squares, 900 rpm. Open and Filled Symbols Are from Runs Made on Two Different Days, Respectively

Possibly the 1-2 seconds subsidence time after stirring and before sheet formation is sufficient to allow recovery of the retention caused by the mechanical stirring. Arvela, et al. (15) have shown that 6 sec was sufficient for complete recovery of retention lost to hydrodynamic shearing when a high molecular weight, high charge density polyamine was used as the retention aid. For that polymer an electrostatic patch mechanism (1) was postulated (15) which should lead to just such behavior. For T5, a moderate molecular weight, low charge density polyelectrolyte, the patch mechanism would appear to be less likely (16) than

a bridging type (17). The recovery of the latter from hydrodynamic disruption would be expected to be much slower than for the patch type interaction. The postulated subsidence time explanation is also not in accord with the continued increase in retention with contact time or with the time scale of many seconds for this increase.

Another possible explanation for the results in Fig. 6 is that 900 rpm may not be sufficient agitation to disrupt retained pigment from the fiber surfaces. It may be worthwhile to study the effect of still higher agitation rates to learn more of the tenacity of retention and its dependence on polymer structure.

For the present the objective was to determine whether the manual agitation was sufficient to bring about the increase in retention with contact time found for the mechanically stirred system. For purposes of efficiency it was desirable to use the former method since the latter required positioning and removing the Lightnin' stirrer each time a sheet was formed so that the sheet could be couched from the wire. In all subsequent experiments manual stirring was used.

The difference in retention (Fig. 6) between the two days is outside the usual variability, but no explanation for it is available at present.

Another factor of interest in these studies was the effect on retention of the flow rate in the mixing tube. For a given length of tube an increase in the flow rate of the furnish produces two effects. First, it decreases the residence time [τ_1 in Equation (3)] in the tube. Second, it increases the collision rate of the particles (fiber and filler) due to the increased rate of turbulent energy dissipation. The amount of retention taking place in the tube is a function of the total number of collisions which is the product of the two

factors just mentioned. Calculations (18) show that the changes in the two factors for the range of variables available to the RMA almost cancel each other with a slight net increase in number of collisions. Experiments (not reported here) in the sheet mold mode do show a very slight increase in retention with increasing flow rate at any given contact time. However, all experiments included in this report in the sheet mold mode were made at the same flow rate and can be unambiguously compared with one another.

In the moving wire mode an additional factor must be considered. Since the stock impinges on the wire at right angles, higher flow rates (i.e., higher $\langle v \rangle$) can cause a greater loss of pigment through the wire. This amounts to 2-3% retention loss (when going from the lower to the higher flow rate) for those systems with polymers that provide only modest retention. On the other hand, for the polymer giving the greatest enhancement of retention, increasing the flow rate of the stock to the moving wire produces an increase of 4-9% in retention. This has important implications with respect to the mechanism of retention and will be discussed further in the following section. In the graphs in this report showing moving wire mode data, the dependence on flow rate (a secondary effect) has been ignored and a smooth curve through all the data points has been used.

Effect of Polymer Structure

Studies of the effectiveness of the six polymeric retention aids were carried out using the RMA over a range of contact times from 0.1 to 70 sec. Whole pulp No. 3 was chosen as a moderately beaten (340 CSF) pulp, and a 5% TiO_2 add-on level was used. Exploratory studies utilizing handsheet formation (Noble and Wood mold) with the stock and the six polymers at various concentrations were made to determine reasonable polymer dosage levels. The results are shown in Fig. 7 as plots of percentage retention of TiO_2 in the sheet against polymer

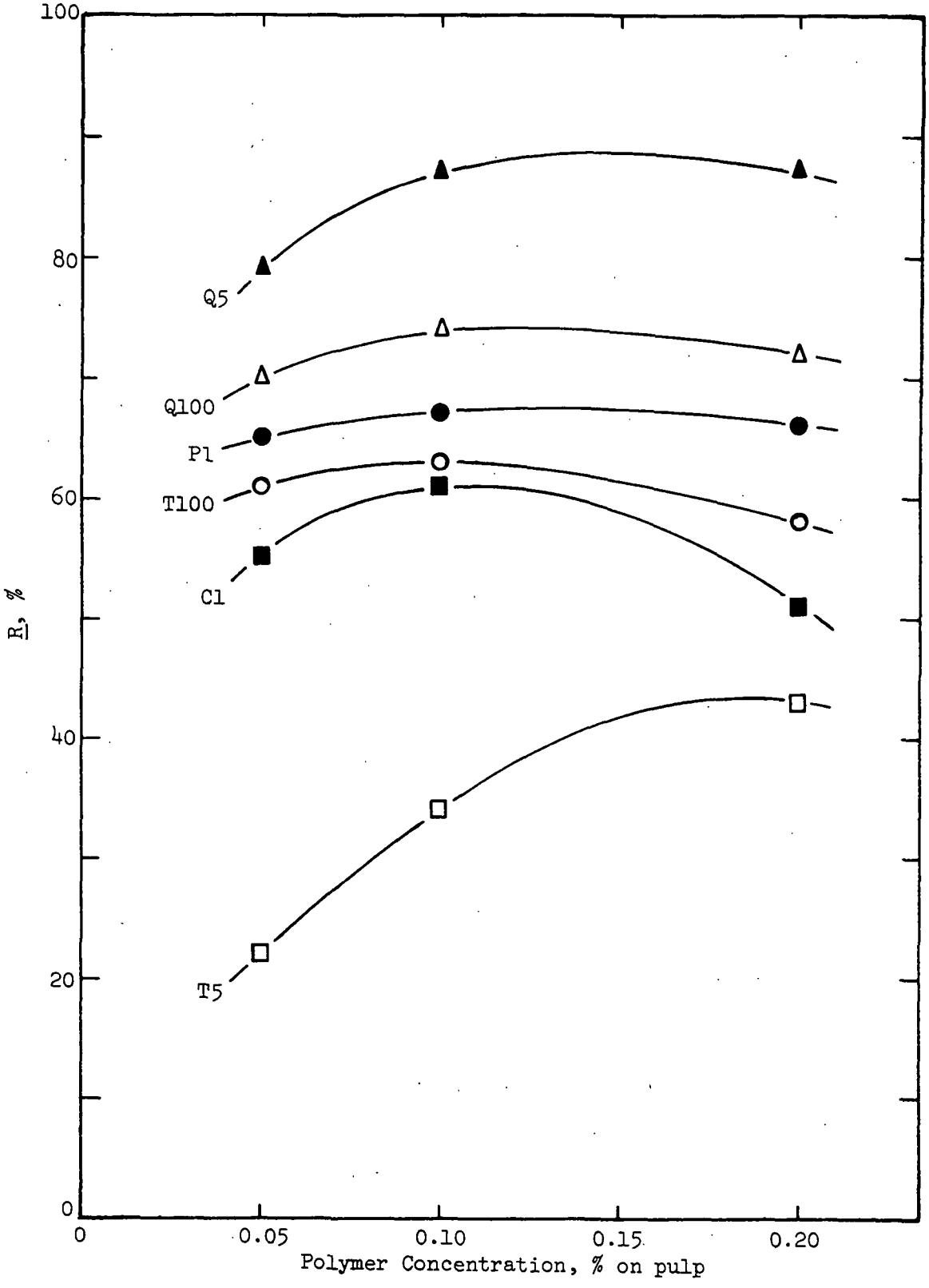

Figure 7. Retention of TiO_2 During Handsheet Formation. 5% TiO_2

concentration. A continuous gradation in effectiveness of the several polymers is observed. Noteworthy is the rather broad concentration range over which the polymers produce good retention. Because 0.1% represents near optimum conditions* for most of the retention aids and is, moreover, a reasonable dosage level (2 lb/ton pulp), this concentration was chosen for most of the subsequent retention experiments.

A summary of the retention experiments is given in Table V. Rather than present all the retention data in tabular or graphic form only the results at selected contact times are given. As will be evident later these are sufficient to define the type of behavior found for a given polymer at a particular concentration. The detailed data in graphical form for several of the runs will be examined more carefully in the following discussion.

The effect of concentration of polymer on retention as a function of contact time is shown in Fig. 8 for T5 and Q100. Several features are immediately evident. The results for the moving wire and sheet mold modes in the region of overlap (contact time of 1 sec) are displaced from one another. However, this is to be expected from the rather different methods of formation in the two cases. The added velocity of the stock impinging at right angles onto the moving wire coupled with the higher drainage forces (higher vacuum in the suction box) lead to a lesser retention here than in the sheet mold mode at the same contact time. Although it would be desirable to have a continuous curve, the results for both modes are reproducible and consistent and their interpretation is not seriously hampered.

*Note added in proof. Recent experiments indicate that the optimum concentration for some polymers on the RMA does not coincide with the value found for the handsheets in Fig. 7.

TABLE V

SUMMARY OF RETENTION EXPERIMENTS

[Pulp No. 3 (whole), 5% TiO_2 on pulp]

Polymer	Conc., % on pulp	Retention, % Moving Wire Contact Time, sec 0.2	Moving Wire 1	Sheet Mold 1	Sheet Mold 10	Sheet Mold 70	ζ, mv	White[a] Water Fines, mg	R, % (hand-sheet)
None	--	8	8	15	15	17	-29	11	--
T5	0.05	10	14	22	29	25	-24	14	22
T5	0.1	12	20	29	39	52	-20	12	34
T5	0.2	13	21	30	39	53	-15	11	43
T5	0.4	--	--	30	35	50	0	11	--
T100	0.1	15	24	30	40	43	+15	12	63
P1	0.1	22	26	37	43	52	+13	11	67
C1	0.03	--	--	42	46	54	+7	10	--
C1	0.1	22	25	34	39	45	+14	13	61
Q5	0.1	43	55	67	79	81	+5	7	87
Q100	0.05	31	42	49	55	62	+5	7	70
Q100	0.1	30	41	53	62	68	+17	3	74

[a] White water fines from sheet mold at 1 sec contact time.

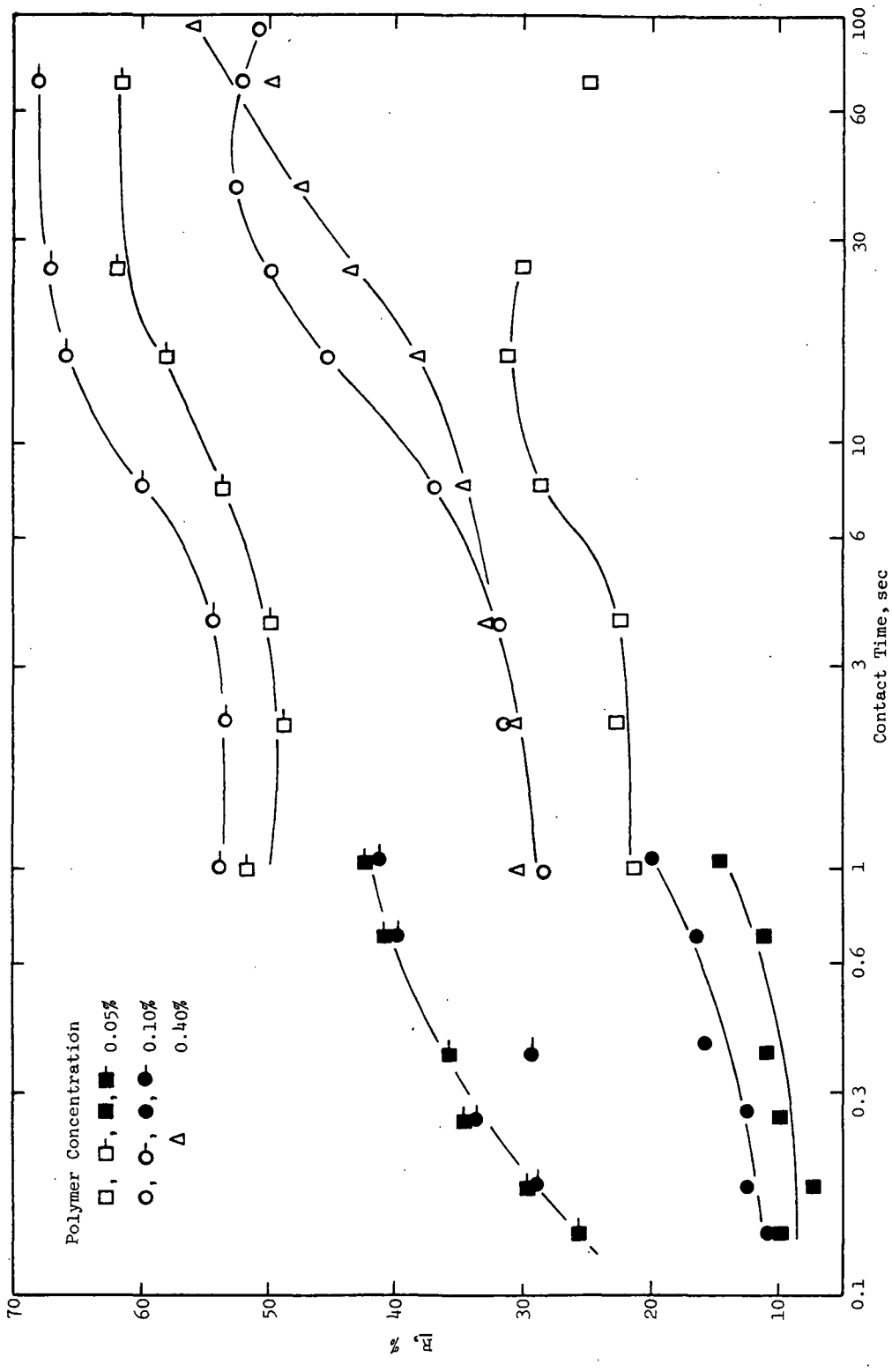

Figure 8. Effect of Concentration of Polymer on Retention. Polymer: Symbols Without Pips, T5; Symbols with Pips, Q100. Filled Symbols, Moving Wire Mode; Open Symbols, Sheet Mold Mode

A logarithmic time scale has been employed because of the orders of magnitude range of this variable. This tends to exaggerate the apparent plateau between 1-2 or 1-4 sec which is a feature of all the curves. It is felt that the plateau is an experimental artifact caused by a lack of agitation of the stock during at least a major fraction of this time. It will be recalled that the lack of agitation here was necessary to ensure good sheet formation. This results in a greatly reduced particle collision rate and, hence, flocculation (or retention) rate during this period.

At long contact times (generally $\geq$ 20-40 sec) a second true plateau is found which represents the maximum retention obtainable. The only exception to this among all six polymers studied was T5. As shown in Fig. 8 a maximum in retention is reached beyond which additional agitation proves detrimental. Apparently the bonds providing the retention with T5 are relatively weak and with time are disrupted. The effect is at least partially irreversible since the 1-2 sec quiescence allowed just prior to sheet formation is not sufficient for recovery. This type of behavior has been discussed by LaMer and Healy (17).

For T5 an increase in concentration from 0.05 to 0.1% provides an increase in retention over the entire range of contact times. Results at 0.2% in the sheet mold mode are virtually identical to those at 0.1% and are not shown in Fig. 8. A further increase in concentration to 0.4% produces an apparent overdose with generally lower retention values. In light of this the point at 95 sec (0.4%) would appear to be out of line. Alternatively, the effect of the overdose may be to shift the development of retention to longer contact times, implying that a smaller fraction of the collisions of pigment and fines (or fiber) was effective in producing coflocculation. This explanation is appealing from the viewpoint of the mechanism of retention but additional

experiments at longer contact times and higher dosages would be necessary for proof.

The results for Q100 presented in Fig. 8 show this polymer to be a more effective retention aid at all contact times. A salient feature is the rather large retention (26%) already present at the shortest contact time measurable ($\sim$0.1 sec). This provides evidence that the adsorption of polymer to an oppositely charged surface is extremely rapid. There is probably little, if any, free polymer remaining in the stock at times $>$0.1 sec. This has important implications for addition of cationic polymers in the mill. Unless extreme care is taken to ensure an even distribution of polymer to all portions of the stock, nonuniform treatment can occur. The latter could lead to inefficient use of the polymer at best and even detrimental effects to sheet physical and optical properties. To obviate this possibility, it may be necessary to introduce the polymer at multiple rather than single points in the stream.

For Q100 at 0.05 and 0.1% the retention on the moving wire is virtually identical. However, at the longer times (and reduced drainage forces) the higher concentration provides greater retention of pigment. It is noteworthy that the final plateau is reached at about the same contact time, implying that the total number of collisions is the important factor here with the final level of retention being related to the amount of particle surface modified by polymer adsorption.

The effect of polymer structure is further explored in Fig. 9. Here the individual data points have been omitted to reduce confusion, using instead smoothed curves. The exception is the base line where no polymer was used. Retention of TiO_2 in that case is conceived to be by a mechanical sieving action and represents the minimum response of the system to which the polymer retention aids add. The discontinuity between the moving wire and sheet mold results is

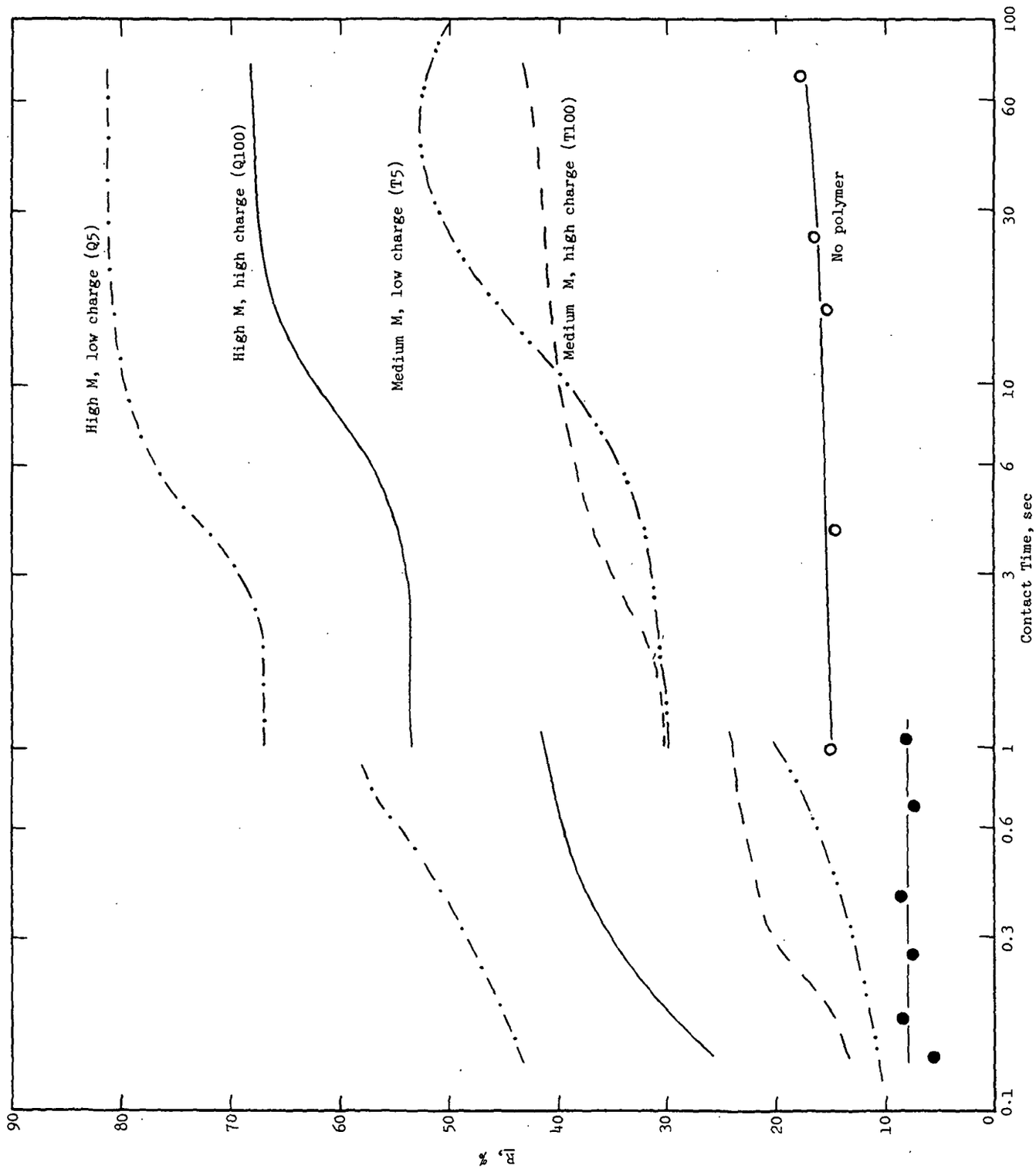

Figure 9. Effect of Polymer Structure on Retention. Polymer Concentration, 0.1%. TiO_2, 5%

present for the base line, also, indicating the stronger drainage forces in the former. The apparent trend of increasing retention with increasing contact time in the sheet mold mode is only just outside experimental error and is probably not a real effect.

The diversity of behavior of the several polymers is considerable. The four polymers can be placed in groups based either on their similar charge density or their similar molecular weight. Two features are immediately apparent. The polymers with high molecular weight are more effective at the given dosage level (0.1%) and a high charge density can be detrimental. Also, the relatively large retention (43%) for Q5 at 0.14 sec is striking, and shows the extreme efficiency of this material. It may also be noted that the change in retention over the range 0.14 to 1 sec is somewhat greater in the case of the high molecular weight polymers than for T5 and T100. Finally, recall that for the moving wire mode for Q5, retention was 4-9% higher at the higher flow rates than for the lower at the same mixing tube length. These several pieces of evidence have implications with regard to the mechanism of coflocculation of the pigment with the fines and fibers.

It is worthwhile at this point to digress momentarily to review the two current theories of flocculation caused by polymers. The first is termed bridging (17) and can apply to nonionic, cationic, or anionic polymers. The physical picture is that of a polymer adsorbed on a particle with long, dangling loops or ends. These latter then can adsorb on empty sites on other particles, thereby forming a physical "bridge." This type of flocculation will be enhanced by increased chain length (molecular weight) of the polymers and in those systems where polymer adsorption in large loops is favored. The equilibrium configuration of the adsorbed polymer chain (i.e., the length of the loops) will depend on the strength of the interaction between the polymer segments and the surface. From

the dependence of saturation adsorption on molecular weight it has been argued (16,19) that a rather flat configuration with few long loops results when a highly charged polymer adsorbs on a surface whose charge is of opposite sign. On the other hand, nonionic and weakly charged polymers have been found (20,21) to have an adsorbed configuration approximating that of an isolated polymer chain in solution, i.e., a random coil. The length of the loops in this case will increase with molecular weight.

The second theory of flocculation, the electrostatic patch theory (1,22), was devised when it was found that strongly charged polymers with relatively flat adsorbed configurations, nonetheless, were quite efficient as flocculants. The physical picture in this case is that of a charged polymer chain adsorbed over a limited area of the particle surface. The amount of charge the polymer conveys to the surface must be greater than the number of surface charges covered by the adsorbed polymer. This leads to an electrostatic patch of sign opposite to that of the uncovered surface which may then exert a strong electrostatic attraction for the uncovered surface of another particle. It is not necessary to neutralize all of the particle's surface charge to get strong flocculation (16,19). Gregory (23) and Eggert (19) have shown that, although the amount of polymer required to achieve the maximum flocculation is independent of molecular weight, polymers with higher molecular weights are more efficient in initiating flocculation than those with shorter chains. On the basis of this evidence they argued that the size of the electrostatic patch was a controlling factor in the early stages of flocculation corresponding to low surface coverage (discrete patches). The patch theory, then, is applicable to polymers with moderate to high charge density adsorbed on a surface of opposite charge. It predicts some dependence on molecular weight, though not as strong as that for the bridging theory.

The various papers mentioned above deal with what can be called equilibrium flocculation. That is, polymer is adsorbed and attains its equilibrium configuration relatively rapidly. This is followed by the flocculation process (either bridging or electrostatic patch interaction), which is governed by the rate of particle collision. Gregory and Sheiham (24) have found evidence that at high particle concentrations ($>10^{11}$ particles/cm^3), a modified behavior which they term "nonequilibrium flocculation" can occur. They argue that a finite time must elapse between the initial contact of a polymer chain with a surface and the attainment of the final equilibrium configuration of that chain. During this time a strongly charged polymer, which will eventually assume a flat configuration and produce (equilibrium) flocculation by an electrostatic patch mechanism, exists in an expanded configuration with large loops and dangling ends. These latter are capable of initiating flocculation by the bridging mechanism if involved in particle collisions during this time. Obviously, polymers with high molecular weight would be much more effective in this type of mechanism than would shorter chains. The other critical parameter here is the particle concentration. There must be sufficient collisions between particles during the nonequilibrium period for bridging to occur. The collision rate is determined by the mean free path of the particles which in turn is a function of the particle concentration and the effective particle diameter. The latter now includes the extension of the polymer chain from the surface. From their results Gregory and Sheiham estimate that equilibrium polymer configuration is attained in about 0.8 to 4 sec.

Returning now to our results on the retention of TiO_2 by the pulp, we find the moving wire and early portions of the sheet mold data to be in the time range estimated for nonequilibrium flocculation. The greatly enhanced retention for high molecular weight polymers, whether of high or low charge

density, is strong supporting evidence for the postulated mechanism. The rapid increase in retention in the moving wire mode for Q5 and Q100 and the obvious dependence on collision rate, mirrored by the increase in retention with increase in flow rate for Q5, further supports this interpretation.

The shape of the curves for times <1 sec provides further evidence. It would be expected that the more strongly charged polymers would reach their equilibrium configuration more quickly than would their counterparts of lower charge density. The concave downward curvature exhibited by the curves for T100 and Q100 in this range suggest that the equilibrium configuration may be reached in about 0.3-0.4 sec. Thereafter the coflocculation proceeds at a slower rate because of the reduced effective diameter of the particles. In contrast, the concave upward curves for T5 and Q5 in this time region suggest that equilibrium configuration is reached only at longer times, probably of the order of a few seconds.

The lower effectiveness of Q100 compared with Q5 at the shortest times may reflect a more advanced stage in the approach to equilibrium for the former and, hence, a lower capability for bridging. Alternatively, it could be the result of a higher molecular weight for Q5 although the intrinsic viscosity results (Table II) indicate otherwise. At long times the higher values with Q5 suggest that bridging molecules anchored by strong electrostatic interaction of adsorbed segments to the surface provide better retention than do strongly charged patches (Q100). A similar effect can be noted for the polymers of moderate molecular weight (T5 and T100).

The retention results for the other polymers with moderate molecular weight and high charge density, C1 and P1, are not shown but closely parallel those for T100 both with respect to shape and magnitude. Apparently, for this

class of polymers (moderate M and high charge density) backbone stiffness and chain geometry (linear or branched) have little effect. This could be anticipated from the postulated mode of coflocculation, the electrostatic patch mechanism, for these materials.

To learn more of the ability of the various polymers to affect the electrochemical properties of the pulp surface, pulp titration measurements were performed. Because of the difficulty in readily clarifying the suspensions with TiO_2 present for electrophoretic mobility measurements, this component (TiO_2) was deleted from the compositions. This would be expected to have little effect on the titration curves since only a minor fraction of the polymer is adsorbed on the TiO_2, the vast majority being adsorbed by the fines due to their large surface area. The results are plotted as zeta potential against polymer concentration in Fig. 10. For clarity smoothed curves have been shown rather than the individual data points. Again, a diversity of behavior is observed with an apparent dependence on molecular weight, charge density, and backbone flexibility. The similar results for the strongly charged polymers near $\zeta=0$ is striking. The exception is C1 which is a factor of 2 more effective in reducing the zeta potential than any of the other polymers. This unusual behavior will be observed again in a later section on freeness, and no explanation is currently available. As expected, the polymers with low charge density, T5 and Q5, are less effective in modifying the charge on the pulp than are the others. It can be conjectured that the greater effect with Q5 than with T5 is a result of the lower molecular weight of the latter which permits it to diffuse into inner regions of the fines and provide only a slight change in the zeta potential. Their being confined to surface regions might also explain the large effect of Q5 and Q100 on the zeta potential at concentrations greater than 0.1%.

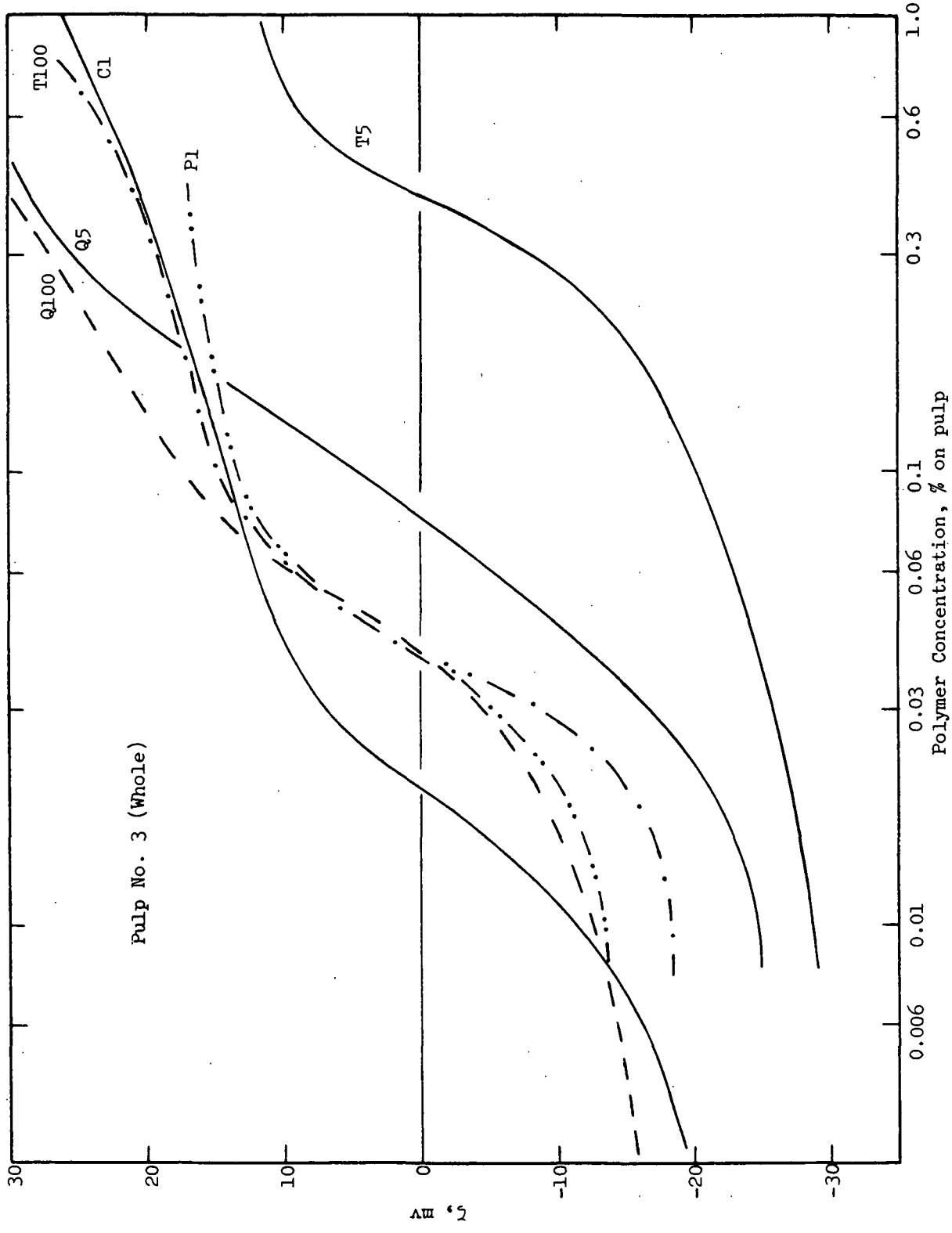

Figure 10. Pulp Titration Curves for Pulp No. 3 (Whole) at pH 5

It is instructive to attempt a correlation of the zeta potential data with the retention results. This can be done by comparing the data in Fig. 10 with those in Fig. 8 and 9 or by comparing the values in Table V of R at a contact time of 70 sec with the values of ζ in the adjacent column. A cursory glance at the latter reveals retentions of 50% or greater at zeta potentials ranging from -20 to +17 mv. Although retention is improved in some cases by making the absolute value of ζ smaller (cf. the two concentrations of C1), the reverse is found for others (cf. the two concentrations of Q100 and the results for T5). Evidently, there is some relationship between zeta potential and retention which is also a function of the mechanism of polymer flocculation. Further work will be required to clarify these interactions.

The relationship between retention in sheets made in a Noble and Wood mold and in the RMA may also be compared in Table V. Except for the results for T5 retentions are 6-20% higher in the hand sheet mold than in the RMA. There are three major differences between the two techniques: 1. The polymer was added to 0.5% consistency pulp for the sheet mold experiments, whereas the consistency in the RMA after mixing was 0.25%. 2. Sheets were formed at 0.04 and 0.25% consistency for the sheet mold and RMA, respectively. 3. The drainage forces are much greater in the case of the RMA. It is not surprising that the correlation is no better than it is. It is expected that the results on the RMA would be more indicative of those to be expected for single pass retention on a paper machine.

For many of the experiments the fines and filler in the white water from both the sheet mold and moving wire modes was measured. As expected, a decrease of TiO_2 in the white water paralleled an increase in retention in the sheet. The data on the fines showed greater scatter, but there was a consistent trend

of increase in white water fines with increasing time for the sheet mold mode. This behavior was finally traced to a classification through the wire of the sheet mold during the contact time while the stock was under agitation in the decklebox. For the case of no polymer added to the furnish the weight of white water fines (for the combined sample from duplicate runs) increased from 11 to 17 mg over the range of contact times of 1 to 70 sec. This corresponds to 2.2 to 3.4% of the total fiber in the furnish compared with the figure of 11.7% total fines as determined by the Bauer-McNett classification procedure. The difference represents the fines retained by sieving during pad formation. For the moving wire mode the average amount of fines lost (no polymer case) was 3.6% of the total fiber with no trend with contact time. The higher amount lost here compared to the sheet mold mode is indicative of the stronger drainage forces on the moving wire.

One series of runs was made with pulp only (no TiO_2). The white water fines for this case was 30% lower than for the series with pulp plus TiO_2. The difference represents the effect of the excess TiO_2 polyphosphate dispersant on fines retention. It has been previously shown (25) that, when the optimum amount of dispersant is used in the original high solids dispersion, a desorption of the dispersant from the TiO_2 surface takes place as the TiO_2 suspension is diluted. At a solids concentration of 125 mg/liter, corresponding to 5% TiO_2 on a 0.25% consistency pulp, the fraction of dispersant bound to the TiO_2 surface is only about 0.1. The excess polyphosphate can adsorb on the fines and reduce their retention in the sheet as it is formed as found above.

For comparison, the white water fines at 1 sec contact time, where the classification phenomenon is minimized, are listed in Table V. The values here for C1, P1, T100, and T5 are equal within experimental error to those for no

polymer (but with TiO_2). Values at longer contact times for these polymers also reproduce the no-polymer case. Also, no effect on fines retention for the moving wire mode was found with P1, C1, T100, and T5. These findings have implications for the mechanism of retention as discussed further in a subsequent section.

Both Q5 and Q100 reduced fines loss 40% or more for both the moving wire and sheet mold modes. Evidently, the high molecular weight of these materials is necessary to form tough bonds by bridging and patch formation, respectively. Considering the whole range of contact times it was found that Q5 was the more effective of the two, further demonstrating the efficacy of bridge formation.

Order of Addition of Components

To gain further insight into the mechanism of retention an experiment was performed where the desired amount of polymer (P1) was mixed with the TiO_2 then adjusted to pH 5 and placed in Reservoir II. The pulp as usual was placed in Reservoir I. This method led to the TiO_2 having its surface almost saturated with highly charged P1 molecules. Even so, the majority of the polymer molecules remained unadsorbed in the TiO_2 slurry. Sheets were then formed as usual at contact times from 1 to 92 sec.

The results are shown in Fig. 11, and are compared there with similar sheets made at the same polymer concentration and the "normal" order of addition (P1 in Reservoir II, pulp plus TiO_2 in Reservoir I). The curves of percentage retention as a function of contact time are strikingly different. For the "reversed order" treatment the retention at 1 sec is 17% or only 2% better than the case where no polymer is added (cf. Fig. 9). Obviously, very little polymer mediated retention has occurred at this point in contrast to 37% retention for

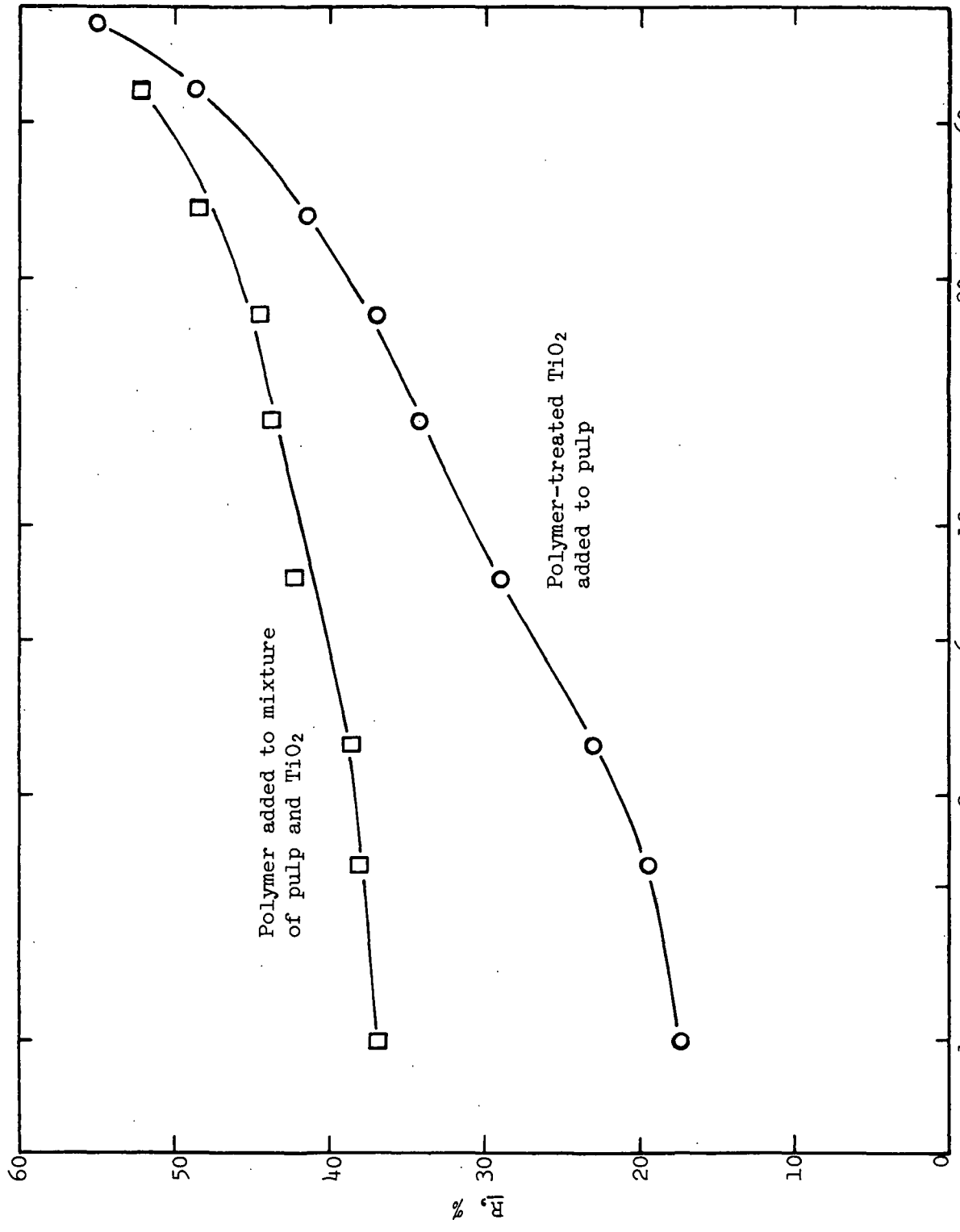

Figure 11. Effect of Order of Addition on Retention. Polymer: 0.1% Pl. 5% TiO_2

the "normal" order of addition. With increasing contact time retention does develop and after about 1-1/2 min the two curves are apparently merging. The proposed explanation for this behavior will be outlined in the next section.

Mechanisms of Retention

In this section we will develop a framework from which to better understand the process of retention. We can write the following heuristic "reactions."

$$F + f + T + p \rightarrow F^* + f^* + T^* \quad \text{(I)}$$

$$F + T^* \rightarrow \overline{FT} \quad \text{(II)}$$

$$f + T^* \rightarrow fT \quad \text{(III)}$$

$$f^* + T^* \rightarrow (fT)^* \quad \text{(IV)}$$

$$F + (fT)^* \rightarrow \overline{FfT} \quad \text{(V)}$$

$$F + fT \rightarrow \overline{FfT} \quad \text{(VI)}$$

The symbols represent, respectively: F, fiber; f, fines; T, TiO_2; p, polymer; F*, f*, T*, the corresponding particle with adsorbed polymer; $\overline{FT}$, TiO_2 adsorbed on fiber; fT, TiO_2 adsorbed on fines; (fT)*, a fine-TiO_2 aggregate with excess adsorbed polymer; $\overline{FfT}$, fiber with adsorbed fines and TiO_2. The "reactions" indicate the interaction of two "particles" to form a third species. Reaction I is the initial extremely rapid step of polymer adsorption onto the various available surfaces. The relative amount of polymer adsorbed on each will be proportional to their respective total surface areas since, over the time scale of this reaction, the particles will be effectively stationary. Polymer adsorption will take place by diffusion to these surfaces and will be governed by the polymer diffusion coefficient. Reactions II and III portray the coflocculation of activated TiO_2 with fiber and fines, respectively. The mechanism of polymer action may be either bridging or electrostatic patch interaction. Reaction IV is similar to III except that the fine possesses a large excess of adsorbed polymer so that the fine-TiO_2

aggregate is capable of further interaction with another surface. In reality, III and IV represent the extremes and fines with moderate amounts of polymer will fall between them and will likely be the usual case. Reaction V shows such an interaction of an "activated" TiO_2-fine aggregate with a fiber surface. Finally, Reaction VI is intended to convey the retention of a fine-TiO_2 aggregate by mechanical sieving during sheet formation. For retention over and above that found for the "no polymer" case, one or more of Reactions II, V, or VI must occur and the product has been overlined to indicate a final retention step.

Reaction II has a lower probability than III for a moderately beaten pulp because of the lower hydrodynamic surface area of a fiber compared with a fine. Reactions III and IV would appear to be the major intermediate step with V and VI the ultimate. It is understood that V can occur either prior to or during drainage.

Next, the evidence of the previous sections will be interpreted in the light of the above reactions. Recall that for polymers C1, P1, T100, and T5 the loss of fines to the white water was not diminished by their presence even though TiO_2 retention was enhanced. This suggests that Reaction V does not occur to an appreciable extent and that the retention of TiO_2 by fiber takes place during drainage <u>via</u> Reaction VI. Of course, the important reaction here is III, the collection of TiO_2 by the fines.

With Q5 and Q100 Reaction V is viable, as reflected by the decrease in white water fines. These large chains are able to coflocculate the fines and fibers by either bridging or formation of large electrostatic patches, respectively. The high molecular weight polymers are necessary to counter the limitations of the large minimum approach distance caused by the irregular surfaces of these particles.

The possibility for both Reactions V and VI to occur leads to the higher retentions found for these materials.

An interpretation for the unusual results of the reverse order of addition experiment can now be advanced. Since Reaction V would not be expected to be probable for P1, the important reactions are III and IV. It is in IV that the trouble arises. Upon mixing in the tee, polymer adsorbs on the fines as usual to create surfaces with positive patches and untreated negative areas. In the present case, however, the surface charge of the TiO_2 is strongly and uniformly positive, rather than having patches like the fines as occurs during normal order of addition. Because of the strongly positive character of the TiO_2, the fraction of near collisions with fines which lead to coflocculation is greatly reduced. Correspondingly, the development of retention (Fig. 11) is a slow process.

Since Reaction III (or IV) is the rate limiting step for the retention process, it is of interest to develop a mathematical model describing it. This is a bimolecular collision process depending on (1) the concentration of TiO_2 particles $[\underline{T}]$ and (2) the concentration of fines times their available surface area. As a first approximation we can assume that this area is in large excess and does not change much during the retention process. We can then write for the fractional decrease in "free" TiO_2 particles with time $\underline{t}$

$$-d([T]/[T]_o)/dt = k[T]/[T]_o \qquad (7)$$

where $[\underline{T}]_o$ is the initial concentration of TiO_2 particles and $\underline{k}$ is the pseudo-first order rate constant embodying the concentration and surface area of the fines, the bimolecular collision frequency, and the collision efficiency. The TiO_2 concentrations can be written in terms of the percentage retention $\underline{R}$.

$$R/100 = 1 - [T]/[T]_o \qquad (8)$$

Upon substituting Equation (8) into (7) and rearranging, we obtain

$$dR/dt = k(100 - R) \qquad (9)$$

Solving this equation yields

$$\log (100 - R) = 2 - kt/2.303 \qquad (10)$$

Equation (10) predicts a linear relationship between the logarithm of (100-R) and time. Data from Fig. 8 and 9 were plotted according to this equation and linear portions were observed at the early times. At longer times the slope (k/2.303) decreased suggesting the original assumption of constant fines surface area becomes a poorer approximation. More detailed data would be required before a quantitative analysis of the retention process in terms of Equation (10) or a modification thereof would be meaningful.

CONCLUSIONS

For retention processes occurring on a short time scale as on a paper machine, the nonequilibrium configuration of adsorbed polymer chains can be an important factor. High molecular weight polymers can provide increased retention through a nonequilibrium coflocculation mechanism.

At the longer contact times (10-20 sec) characteristic of paper machine operation high molecular weight polymers ($M \geq 10^6$) enhance retention by coflocculation of fines with fibers. A polymer of relatively low charge density can be more effective than one with high charge density presumably because of its larger sphere of influence (long loops for bridging).

Polymers of moderate molecular weight do not improve fines retention. The parameters of backbone stiffness and chain geometry appear to exert only a secondary influence on the behavior of the retention aid.

DRAINAGE STUDIES

The goal of these studies was to determine the effect of polymeric drainage aids on the basic pulp properties, and to relate the efficiency of the various polymers to their molecular architecture. To this end a series of polymer-treated pulps were subjected to constant-rate filtration testing.

EXPERIMENTAL

Since the largest effects on drainage improvement are to be expected for highly beaten pulps, the classified and whole samples of pulp No. 4 were used for this study. The pulp was disintegrated in 30-g batches at 2% consistency in the British disintegrator for 300 counts and then diluted to 0.5% consistency. Aliquots containing 10 g of pulp were treated with the desired dosage of polymer while being stirred with a Lightnin' mixer. The 0.1% polymer solution was added slowly to the agitated pulp, and stirring was continued for 5 min after addition. The treated pulps were stored overnight and tested the next day.

Exploratory studies showed no change in Canadian freeness and little change in zeta potential on pulp samples measured immediately after treatment with the polymer and 16-20 hours later.

The experimental techniques and apparatus used in carrying out a constant-rate filtration have been previously described (26,27). The 0.5% consistency pulp was deaerated under vacuum and diluted to about 0.01% consistency. It was then introduced into a filtration tube assembly and a constant rate of flow was maintained through a screen by a variable speed gear pump discharging through a rotameter. As the filtration proceeded and mat thickness built up on the supporting septum (150-mesh screen), the pressure drop across the mat was measured as a function of time by a differential pressure cell and strip chart recorder.

The compressibility of the fibers was measured in a second experiment. The pseudo-equilibrium compression response was established by static loading a permeable piston surmounting a fiber mat and measuring the piston deflection as a function of load. The pad concentration C_p was then calculated from pad dimensions and weight and is related to the compacting load by

$$C_p = MP^N \tag{11}$$

where P is the compacting load in dynes/cm^2 and M and N are empirical constants in consistent cgs units.

ANALYSIS OF CONSTANT-RATE FILTRATION DATA

The filtration resistance is calculated from a form of the Darcy equation applicable to compressible media

$$R = \frac{A^2}{(dv/d\theta)^2 \mu C} \cdot \frac{\Delta P_f}{\theta} = B \cdot \frac{\Delta P_f}{\theta} \tag{12}$$

where

R = average specific filtration resistance, cm/g

A = cross-sectional area of flow, cm^2

ΔP_f = overall frictional pressure drop, dynes/cm^2

$dv/d\theta$ = volumetric rate of flow, cm^3/sec

μ = filtrate viscosity, poise

θ = time of filtration, sec

C = mass of fibers deposited in the bed per unit volume of filtrate, g/cm^3

B = filtration constant, cgs units

The superficial velocity through the fiber bed must be maintained in the viscous regime, i.e., 2 cm/sec or less. At these low flow rates, the pressure drop across the septum may be neglected.

Fiber specific surface S_w and specific volume v may be calculated from a form of the Kozeny-Carman equation (28)

$$\frac{\Delta P_f}{\theta C_p^{1/2}} = \frac{3.5(1-n/2)S_w^2}{Bv^{1/2}} \{1 + 57\, C_p^3[(1-n/2)^2 v]^3\} \qquad (13)$$

If the left-hand side of Equation (13) is plotted against C_p^3, the slope and intercept from a linear fit of the data may be used to calculate the hydrodynamic specific surface and specific volume. The accuracy in determining these parameters by this method is 1-2%.

RESULTS AND DISCUSSION

Effect of Polymer Structure on Freeness

The predominant theory (29-31) for the action of drainage aids is that the polymer effects retention of the pulp fines onto the fibers, thereby forming a sheet with an open network of pores. These latter provide channels for good drainage and for water removal in the presses, and facilitate evaporation in the driers. Ellis and Foster (30) have shown by micrographs dramatic evidence of the coflocculation of fines and fibers engendered by a polymeric aid.

Recently, Moore (32) has measured the drainage properties of a classified pulp treated with a cationic polymer and alum. Substantial increases in freeness and permeability were found. It is evident that the fines flocculation mechanism is inoperative here and that other possibilities must be considered.

To roughly gage the effectiveness of the various polymers as drainage aids, Canadian freeness was measured as a function of dosage. The results are shown in Fig. 12 for both the whole and classified pulps. In agreement with Moore (32), an increase in freeness was found for the classified pulp. For the whole pulp a variety of behavior was found ranging from little effect, to

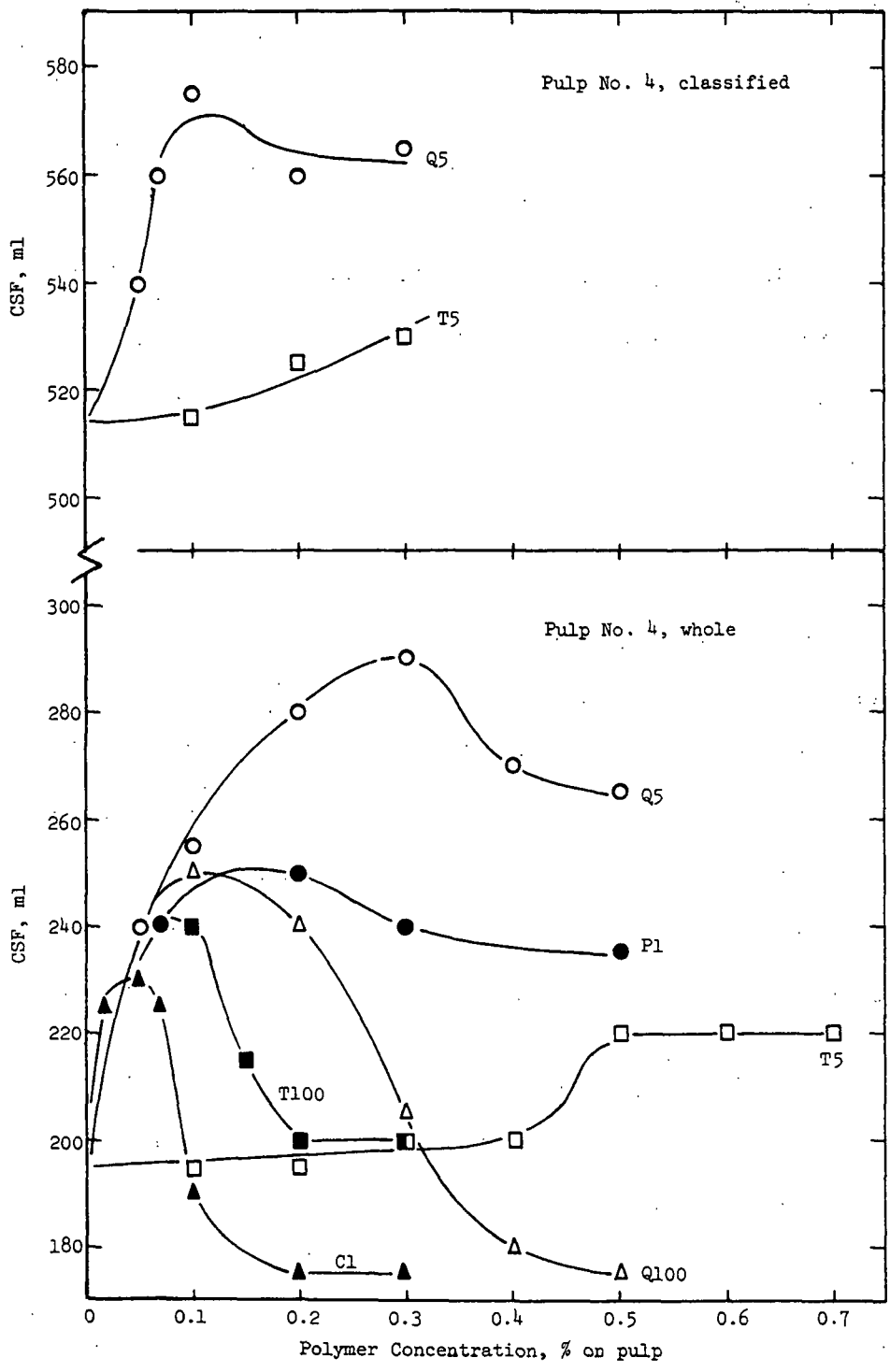

Figure 12. Effect of Polymer Structure on Freeness in Deionized Water Adjusted to pH 5

a strong increase in freeness, to a decrease in freeness with overdosage. The peculiar ability of C1 to effect changes at very low concentrations can again be noted. The strong effect of molecular weight can again be observed in the behavior of T5 vis-à-vis that of Q5. For the polymers of higher charge density the difference is much smaller (cf. T100 with Q100).

Filtration Resistance Results

The filtrations were carried out in distilled water adjusted to pH 5 with H_2SO_4. The results for eight samples (four whole and four classified pulps) are discussed in this report. Included are the base-line stock and three samples treated with different polymers at a 0.1% dosage level. Typical filtration resistance curves are presented in Fig. 13 for the base stock and for the sample treated with 0.1% Q5. In these measurements the classified pulp showed an even larger effect upon treatment than did the whole pulp. This is further evidence that fines coflocculation is not the only mechanism in drainage improvement.

Compressibility data on both the whole and classified pulp were the same and yielded the constants: $M = 0.0018$, $N = 0.396$. Combining these results with the filtration resistance values, the data were analyzed using Equation (13) to yield S_w and v. The results are listed in Table VI.

The values for filtration resistance bear out the trends observed in Fig. 12 for these three polymers. That is, at the 0.1% level, Q5 and P1 give approximately equal reduction in resistance, while T5 has little, if any, effect. Polymers Q5 and P1 provide a decrease (from the values of the base stock) in S_w and no change in specific volume for both the whole and classified pulps. The difference in the value for S_w for T5 compared with the base stock is zero within experimental error.

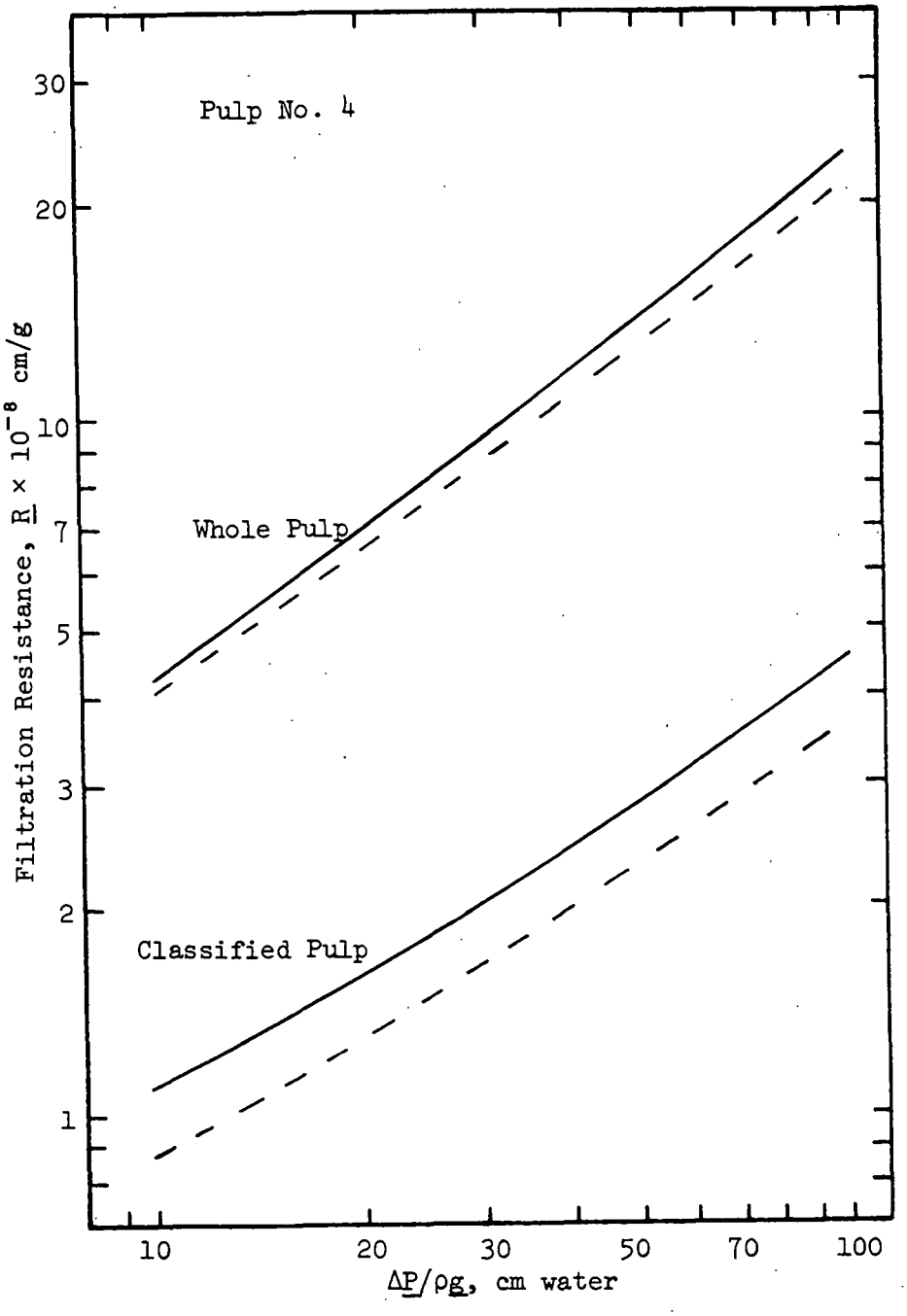

Figure 13. Effect of Polymer on Constant Rate Filtration. Solid Line, no Additive; Broken Line, 0.1% Q5

TABLE VI

CONSTANT-RATE FILTRATION PARAMETERS

Polymer	Conc., % on pulp	Filtration Resistance $\underline{R} \times 10^{-8}$, cm/g (Pressure Drop = 10 cm H_2O)	$\underline{S}_w$, cm^2/g	$\underline{V}$, cm^3/g	CSF, ml	ζ, mv
		Classified Pulp No. 4				
None	--	1.10	16,750	2.57	515	-21
Q5	0.1	0.88	15,000	2.62	575	-22
T5	0.1	1.00	16,150	2.61	515	-20
P1	0.1	0.94	15,150	2.56	570	--
		Whole Pulp No. 4				
None	--	4.20	35,200	2.90	195	-26
Q5	0.1	4.10	34,000	2.86	255	-16
T5	0.1	4.52	36,700	2.96	195	-18
P1	0.1	3.99	34,500	2.87	250	-16

The typically highly-fibrillated surfaces of well-beaten fibers may be considered to exist in that state due to (1) mutual repulsion of the negatively charged fibrils and fibers or (2) to the presence of strong hydration sheaths about the fibrils. Polymers can reduce the fibrillation due to (1) by either a charge neutralization or bridging mechanism. Pendrich (33) has suggested that the drainage aid may decrease the hydration of the cellulose fibers. The constancy of the specific volume results in Table VI indicate this explanation is not viable for the samples studied here. The rather sizeable negative zeta potentials for these systems imply that charge neutralization is not a major factor in the freeness enhancement. Further work will be required to characterize and define the operative mechanisms.

CONCLUSIONS

Constant-rate filtration data can identify the effects of polymer additives on pulp properties. Changes in drainage can be traced to modification of the fiber specific surface area but not specific volume. Coflocculation of fines is not the only mechanism for drainage improvement.

FUTURE WORK

The remainder of Phases I and II will be carried out during the balance of the first year of the project. In the area of retention the following experiments are planned.

a) Studies of clay retention and comparison with TiO_2 behavior.

b) Studies of classified pulp to further define the role of fines.

c) Studies of the effect of degree of refining on retention.

The drainage studies will be concentrated on defining more clearly the effects of polymers on pulp properties and in correlating these with polymer structure. Examination of the effect of different levels of fines added to a classified pulp may further illuminate the relative role of fines coflocculation in drainage improvement.

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LITERATURE CITED

1. Gregory, J., J. Colloid Interface Sci. 42:448(1973).

2. Dick, C. R., and Ham, G. E., J. Macromol. Sci.-Chem. A4(6):1301(1970).

3. Tanford, C. Physical chemistry of macromolecules. New York, Wiley, 1961.

4. Katchalsky, A., Mazur, J., and Spitnik, P., J. Polymer Sci. 23:513(1957).

5. Bloys van Treslong, C. J., and Staverman, A. J., Rec. Trav. Chim. 93:171 (1974).

6. Lindquist, G. M. Doctoral Dissertation. Appleton, WI, The Institute of Paper Chemistry, 1974.

7. Webb, J. T. Doctoral Dissertation. Appleton, WI, The Institute of Paper Chemistry, 1971.

8. Holtzman, W. Doctoral Dissertation. Appleton, WI, The Institute of Paper Chemistry, 1959.

9. Caldin, E. F. Fast reactions in solution. New York, Wiley, 1964.

10. Andrews, B. D. Personal communication, 1976.

11. Overbeek, J. Th. G. Electrokinetic phenomena. In Kruyt's Colloid science. Vol. 1. p. 194. New York, Elsevier, 1952.

12. Britt, K. W., Tappi 56(10):46(1973).

13. Lodzinski, F. P. Private communication, 1976.

14. Arnson, T. R. Unpublished work, The Institute of Paper Chemistry, 1976.

15. Arvela, P., Swanson, J. W., and Stratton, R. A., Tappi 58(11):86(1975).

16. Lindquist, G. M., and Stratton, R. A., J. Colloid Interface Sci., In press.

17. LaMer, V. K., and Healy, T. W., Rev. Pure Appl. Chem. 13:112(1963).

18. Stratton, R. A. Unpublished work, The Institute of Paper Chemistry, 1976.

19. Eggert, A. R. Doctoral Dissertation. Appleton, WI, The Institute of Paper Chemistry, 1976.

20. Garvey, M. J., Tadros, Th. F., and Vincent, B., J. Colloid Interface Sci. 49:57(1974).

21. Fleer, G. J., Koopal, L. K., and Lyklema, J., Kolloid-Z. u. Z. Polymere 250:689(1972).

22. Kasper, D. R. Doctoral Dissertation. Pasadena, CA, California Institute of Technology, 1971.

23. Gregory, J. Paper presented at 49th National Colloid Symposium, Potsdam, New York, June 16-18, 1975.

24. Gregory, J., and Sheiham, I., Brit. Polymer J. 6:47(1974).

25. Stratton, R. A., Baum, G. A., and Swanson, J. W. A fundamental study of polymer flocculation and retention aids. Progress Report Four, Project 3143, Appleton, WI, The Institute of Paper Chemistry, January 20, 1975.

26. Ingmanson, W. L., Tappi 35(10):439(1952).

27. Ingmanson, W. L., and Andrews, B. D., Tappi 42(1):29(1959).

28. Ingmanson, W. L., and Andrews, B. D., Tappi 46(3):150(1963).

29. Poschmann, F. J., Pulp Paper Mag. Can. 69(8):59(1968).

30. Ellis, W. H., and Foster, W. A., Paper Trade J. 152(23):34(1968).

31. Linke, W. F., Tappi 51(11):59A(1968).

32. Moore, E. E., Tappi 58(1):99(1975).

33. Pendrich, T. W. E., Paper 180(5):291(1973).

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